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AN UNDULATORY THEORY OF THE MECHANICS OF ATOMS AND MOLECULES

By E. Schrödinger

Abstract

The paper gives an account of the author's work on a new form of quantum theory. §1. The Hamiltonian analogy between mechanics and optics. §2. The analogy is to be extended to include real "physical" or "undulatory" mechanics instead of mere geometrical mechanics. §3. The significance of wave-length; macro-mechanical and micro-mechanical problems. §4. The wave-equation and its application to the hydrogen atom. §5. The intrinsic reason for the appearance of discrete characteristic frequencies. §6. Other problems; intensity of emitted light. §7. The wave-equation derived from a Hamiltonian variation-principle; generalization to an arbitrary conservative system. §8. The wave-function physically means and determines a continuous distribution of electricity in space, the fluctuations of which determine the radiation by the laws of ordinary electrodynamics. §9. Non-conservative systems. Theory of dispersion and scattering and of the "transitions" between the "stationary states." §10. The question of relativity and the action of a magnetic field. Incompleteness of that part of the theory.

1. The theory which is reported in the following pages is based on the very interesting and fundamental researches of L. de Broglie[1] on what he called "phase-waves" ("ondes de phase") and thought to be associated with the motion of material points, especially with the motion of an electron or proton. The point of view taken here, which was first published in a series of German papers,[2] is rather that material points consist of, or are nothing but, wave-systems. This extreme conception may be wrong, indeed it does not offer as yet the slightest explanation of why only such wave-systems seem to be realized in nature as correspond to mass-points of definite mass and charge. On the other hand the opposite point of view, which neglects altogether the waves discovered by L. de Broglie and treats only the motion of material points, has led to such grave difficulties in the theory of atomic mechanics

[1] L. de Broglie, Ann. de Physique **3**, 22 (1925).

[2] E. Schrödinger, Ann. d. Physik **79**, 361, 489, 734; **80**, 437 **81**, 109 (1926); Die Naturwissenschaften **14**, 664 (1926).

—and this after century-long development and refinement—that it seems not only not dangerous but even desirable, for a time at least, to lay an exaggerated stress on its counterpart. In doing this we must of course realize that a thorough correlation of all features of physical phenomena can probably be afforded only by a harmonic union of these two extremes.

The chief advantages of the present wave-theory are the following.

a. The laws of motion and the quantum conditions are deduced simultaneously from one simple Hamiltonian principle.

b. The discrepancy hitherto existing in quantum theory between the frequency of motion and the frequency of emission disappears in so far as the latter frequencies coincide with the differences of the former. A definite localization of the electric charge in space and time can be associated with the wave-system and this with the aid of ordinary electrodynamics accounts for the frequencies, intensities and polarizations of the emitted light and makes superfluous all sorts of correspondence and selection principles.

c. It seems possible by the new theory to pursue in all detail the so-called "transitions," which up to date have been wholly mysterious.

d. There are several instances of disagreement between the new theory and the older one as to the particular values of the energy or frequency levels. In these cases it is the new theory that is better supported by experiment.

To explain the main lines of thought, I will take as an example of a mechanical system a material point, mass m, moving in a conservative field of force $V(x, y, z)$. All the following treatment may very easily be extended to the motion of the "image-point," picturing the motion of a wholly arbitrary conservative system in its "configuration-space" (q-space, not pq-space). We shall effect this generalization in a somewhat different manner in Section 7. Using the usual notations the kinetic energy T is

$$T=\tfrac{1}{2}m(\dot{x}^2+\dot{y}^2+\dot{z}^2)=(1/2m)(p_x^2+p_y^2+p_z^2). \tag{1}$$

The well-known Hamiltonian function of action W,

$$W=\int_{t_0}^{t}(T-V)dt, \tag{2}$$

taken as a function of the upper limit t and of the final values of the coordinates x, y, z satisfies the Hamiltonian partial differential equation,

$$\partial W/\partial t+(1/2m)[(\partial W/\partial x)^2+(\partial W/\partial y)^2+(\partial W/\partial z)^2]+V(x,y,z,)=0. \tag{3}$$

To solve this equation, we put as usual

$$W = -Et + S(x, y, z), \tag{4}$$

E being an integration constant, viz., the total energy, and S a function of x, y, z only. Eq. (3) may then be written

$$|\operatorname{grad} W| = [2m(E-V)]^{\frac{1}{2}}. \tag{5}$$

In this form it lends itself to a very simple geometrical interpretation. Assume t constant for the moment. Any function W of space alone can be described by giving geometrically the system of surfaces on which W is constant and by writing down on each one of these surfaces the constant value, say W_0, which the function W takes on it. On the other hand, we can easily construct a solution of Eq. (5) starting from an arbitrary surface and an arbitrarily chosen value W_0, which we ascribe to it. For after having chosen starting surface and starting value and after—still arbitrarily—having designated one of its two sides or "shores" as the positive one, we simply have to extend the normal at every point of the chosen surface to the length, say

$$dn = dW_0/[2m(E-V)]^{\frac{1}{2}}.$$

The totality of points arrived at in this way will fill a surface to which we obviously have to ascribe the value W_0+dW_0. The continuation of this procedure will supply us the whole system of surfaces and values of constants belonging to them, i.e. the whole distribution in space of the function W, at first for t constant.

Now let the time vary, Eq. (4) shows that the system of surfaces will not vary, but that the values of the constants will travel along the normals from surface to surface with a certain speed u, given by

$$u = E/[2m(E-V)]^{\frac{1}{2}}. \tag{6}$$

The velocity u is a function of the energy-constant E and besides, since it contains $V(x,y,z)$ is a function of the coordinates.

Instead of thinking of the surfaces as fixed in space and letting the values of the constant wander from surface to surface, we may equally well think of a certain numerical value of W as attached to a certain individual surface and let the surfaces wander in such a way that each of them continually takes the place and exact form of the following one. Then the quantity u, given by Eq. (6) will denote the normal-velocity of any surface at any one of its points. Adopting this view we arrive at a picture which exactly coincides with the propagation of a stationary wave-system in an optically non-homogeneous (but isotropic)

medium, W being proportional to the phase and u being the phase-velocity. (The index of refraction would have to be taken proportional to u^{-1}.) The above-mentioned construction of normals dn is obviously equivalent to Huygens' principle. The orthogonal curves of our system of W-surfaces form a system of rays in our optical picture; they are possible orbits of the material point in the mechanical problem. Indeed it is well known that

$$p_x = m\dot{x} = \partial W/\partial x \tag{7}$$

(with two analogous equations for y and z). It may be useful, to remark, that the phase-velocity u is not the velocity of the material point. The latter is, by (7) and (5)

$$v = (\dot{x}^2+\dot{y}^2+\dot{z}^2)^{\frac{1}{2}} = [2(E-V)/m]^{\frac{1}{2}}. \tag{8}$$

Comparing (6) and (8) we see, that u and v vary even inversely to each other. The well-known mechanical principle due to and named after Hamilton can very easily be shown to correspond to the equally well-known optical principle of Fermat.

2. Nothing of what has hitherto been said is in any way new. All this was very much better known to Hamilton himself than it is in our day to a good many physicists. Indeed, the theory of the propagation of light in a non-homogeneous medium, which Hamilton had developed about ten years earlier, became, by the striking analogy which occurred to him, the starting-point for his famous theories in pure mechanics. Notwithstanding the great popularity reached by the latter, the way which had led to them was nearly forgotten.[3] Stress must now be laid on the fact, that though in our above-stated reasoning such conceptions as "wave-surfaces," "Huygens' principle," "Fermat's principle" come into play, nevertheless the whole established analogy deals rather with geometrical optics than with real physical or undulatory optics. Indeed the chief and fundamental mechanical conception is that of the path or orbit of the material particle, and it corresponds to the conception of rays in the optical analogy. Now the conception of rays is thoroughly well-defined only in pure abstract geometrical optics. It loses nearly all significance in real physical optics as soon as the dimensions of the beam or of material obstacles in its path become comparable with the wave-length. And even when this is not the case, the notion of rays is, in

[3] See F. Klein, Jahresber. d. Deutsch. Math. Ver. 1 (1891); Zeits. f. Math. u. Phys. **46** (1901); (Ges. Abh. II, 601, 603); E. T. Whittaker, Analytical Dynamics, Chap. 11. A. Sommerfeld, Atombau, German ed., p. 803. The analogy has been rediscovered in relativistic mechanics in the paper of L. de Broglie, quoted above.

physical optics, merely an approximate one. It is wholly incapable of being applied to the fine structure of real optical phenomena, i.e. to the phenomena of diffraction. Even in extending geometrical optics somewhat by adding the notion of Huygens' principle (in the simple form, used above) one is not able to account for the most simple phenomena of diffraction without adding some further very strange rules concerning the circumstances under which Huygens' envelope-surface is or is not physically significant. (I mean the construction of "Fresnel's zones.") These rules would be wholly incomprehensible to one versed in geometrical optics alone. Furthermore it may be observed that the notions which are fundamental to real physical optics, i.e. the wave-function itself (W is merely the phase), the equation of wave-propagation, the wave-length and frequency of the waves, do not enter at all into the above stated analogy. The phase-velocity u does enter but we have seen that it is not very intimately connected with the mechanical velocity v.

At first sight it does not seem at all tempting, to work out in detail the Hamiltonian analogy as in real undulatory optics. By giving the wave-length a proper well-defined meaning, the well-defined meaning of rays is lost at least in some cases, and by this the analogy would seem to be weakened or even to be wholly destroyed for those cases in which the dimensions of the mechanical orbits or their radii of curvature become comparable with the wave-length. To save the analogy it would seem necessary to attribute an exceedingly small value to the wave-length, small in comparison with all dimensions that may ever become of any interest in the mechanical problem. But then again the working out of an undulatory picture would seem superfluous, for geometrical optics is the real limiting case of undulatory optics for vanishing wave-length.[4]

Now compare with these considerations the very striking fact, of which we have today irrefutable knowledge, that ordinary mechanics is really not applicable to mechanical systems of very small, viz. of atomic dimensions. Taking into account this fact, which impresses its stamp upon all modern physical reasoning, is one not greatly tempted to investigate whether the non-applicability of ordinary mechanics to micro-mechanical problems is perhaps of exactly the same kind as the non-applicability of geometrical optics to the phenomena of diffraction or interference and may, perhaps, be overcome in an exactly similar way? The conception is: the Hamiltonian analogy has really to be worked out towards undulatory optics and a definite size is to be at-

[4] A. Sommerfeld and I. Runge, Ann. d. Physik **35**, 290 (1911).

tributed to the wave-length in every special case. This quantity has a real meaning for the mechanical problem, viz. that ordinary mechanics with its conception of a moving point and its linear path (or more generally of an "image-point" moving in the coordinate space) is only approximately applicable so long as they supply a path, which is (and whose radii of curvature are) large in comparison with the wave-length. If this is not the case, it is a phenomenon of wave-propagation that has to be studied. In the simple case of one material point moving in an external field of force the wave-phenomenon may be thought of as taking place in the ordinary three-dimensional space; in the case of a more general mechanical system it will primarily be located in the coordinate space (q-space, not pq-space) and will have to be projected somehow into ordinary space. At any rate the equations of ordinary mechanics will be of no more use for the study of these micro-mechanical wave-phenomena than the rules of geometrical optics are for the study of diffraction phenomena. Well known methods of wave-theory, somewhat generalized, lend themselves readily. The conceptions, roughly sketched in the preceding are fully justified by the success which has attended their development.

3. Let us return to the system of W-surfaces, dealt with in Section 1 and let us associate with them the idea of stationary sinusoidal waves whose phase is given by the quantity W, Eq. (4). The wave-function, say ψ, will be of the form

$$\begin{aligned}\psi &= A(x,y,z)\sin(W/K) \\ &= A(x,y,z)\sin\left[-Et/K+S(x,y,z)/K\right],\end{aligned} \tag{9}$$

A being an "amplitude" function. The constant K must be introduced and must have the physical dimension of *action* (energy$\times$time), since the argument of a sine must always be a pure number. Now, since the frequency of the wave (9) is obviously

$$\nu = E/2\pi K \tag{10}$$

one cannot resist the temptation of supposing K to be a *universal constant*, independent of E and independent of the nature of the mechanical system, because if this be done and K be given the value $h/2\pi$, then the frequency ν will be given by

$$\nu = E/h, \tag{11}$$

h being Planck's constant. Thus the well known universal relation between energy and frequency is arrived at in a rather simple and unforced way.

In ordinary mechanics the absolute value of the energy has no definite meaning, only energy-differences have. This difficulty can be met and a zero-level of energy can be defined in an entirely satisfactory way by using relativistic mechanics and the conception of equivalence of mass and energy.[1] But it is unnecessary to dwell on this subject here. While the frequency ν of our waves by Eq. (10) or (11) is indeed dependent on the zero-level of energy, their wave-length is not. And after what has been said above, it is the wave-length that is of greatest interest. The comparison of this quantity with the dimensions of the path or orbit of the material particle, calculated according to ordinary mechanics, will tell us whether the latter calculation is or is not of physical significance, whether the methods of ordinary mechanics are approximately applicable to the special problem or not. The wave-length λ by (11) and (6) is

$$\lambda = u/\nu = h/[2m(E-V)]^{\frac{1}{2}} \tag{12}$$

Here $E-V$ is the kinetic energy $\frac{1}{2}mv^2$ which indeed is independent of the zero-level of the total energy. Inserting its value we have

$$\lambda = h/mv. \tag{13}$$

To test the question whether an electron, moving in a Keplerian orbit of atomic dimensions may, following our hypotheses, still be dealt with by ordinary mechanics, let a be a length of atomic dimensions and compare λ with a.

$$\lambda/a = h/mva \tag{14}$$

The denominator on the right is certainly of the order of magnitude of the moment of momentum of the electron, and the latter is well known to be of the order of magnitude of Planck's constant for a Keplerian orbit of atomic dimensions. So λ/a becomes of the order of unity and, following our conceptions, ordinary mechanics will be no more applicable to such an orbit than geometrical optics is to the diffraction of light by a disk of diameter equal to the wave-length. Were a physicist to try to understand the latter phenomenon by the conception of rays, with which he is acquainted from macroscopic geometrical optics, he would meet with most serious difficulties and apparent contradictions. The "rays" (stream lines of the flow of energy) would no longer be rectilinear and would influence one another in a most curious way, in full contradiction with the most fundamental laws of geometrical optics. In the same way the conception of orbits of material points seems to be inapplicable to orbits of atomic dimensions. It is very satisfactory, that the limit of applicability of ordinary mechanics is, by equating K (essentially)

to Planck's constant (Eq. 11), determined to an order of magnitude, which is exactly the one to be postulated, if the new conception is to help us in our quantum difficulties. We may add, that by Eq. (13) for a Keplerian electronic orbit of the order of magnitude of a high quantum orbit, the relation of wave-length to orbital dimensions becomes of the order of magnitude of the reciprocal of the quantum number. Hence ordinary mechanics will offer a better and better approximation in the limit of increasing quantum number (or orbital dimensions), and this is just what is to be expected from any reasonable theory.

By the fundamental equation $\nu = E/h$ (Eq. 11) the phase velocity u, given by Eq. (6) proves to be dependent on the frequency ν. Therefore Eq. (6) is an equation of dispersion. By this a very interesting light is thrown on the relation of the two velocities (1) velocity v of the moving particle, Eq. (8); (2) phase-velocity u, Eq. (6). v is easily proved to be exactly the so-called group velocity belonging to the dispersion formula (6).[5] By using this interesting result it is possible to form an idea how ordinary mechanics is capable of giving an approximate description of our wave motion. By superposing waves of frequencies in a small interval ν; $\nu+d\nu$ it is possible to construct a "parcel of waves," the dimensions of which are in all directions rather small, though they must be rather large in comparison to the wave-length. Now it can be proved, that the motion of—let us say—the "center of gravity" of such a parcel will, by the laws of wave propagation, follow exactly the same orbit as the material point would by the laws of ordinary mechanics. This equivalence is always maintained, even if the dimensions of the orbit are not large in comparison with the wave-length. But in the latter case it will have no significance, the wave parcel being spread out in all directions far over the range of the orbit. On the contrary, if the dimensions of the orbit are comparatively large, the motion of the wave parcel as a whole may afford a sufficient idea of what really happens, if we are not interested in its intrinsic constitution. As stated above this "motion as a whole" is governed by the laws of ordinary mechanics.

4. We shall not dwell on this question further, but proceed to the far more interesting applications of the theory to micro-mechanical problems. As stated above, the wave-phenomena must in this case be studied in detail. This can only be done by using an "equation of wave propagation." Which one is this to be? In the case of a single material point, moving in an external field of force, the simplest way is to try to use the ordinary wave-equation

[5] This important theorem is due to L. de Broglie, l.c. The relation is: $v = d\nu/d(\nu/u)$

$$\Delta\psi - \ddot{\psi}/u^2 = 0 \tag{15}$$

and to insert for u the quantity given by Eq. (6), which depends on the space coordinates (through the potential energy V) and on the frequency E/h. The latter dependence restricts the use of (15) to such functions ψ as depend on the time only through the factor $e^{\pm 2\pi i t E/h}$. (A similar restriction is always imposed on the wave equation, as soon as we have dispersion.) So we shall have

$$\ddot{\psi} = -4\pi^2 E^2 \psi / h^2$$

Inserting this and Eq. (6) in Eq. (15) we get

$$\Delta\psi + 8\pi^2 m(E-V)\psi/h^2 = 0, \tag{16}$$

where ψ may be assumed to depend on x, y, z only. (We omit changing the notation of the dependent variable, which we really ought to do.)

Now what are we to do with Eq. (16)? At first sight this equation seems to offer ill means of solving atomic problems, e.g. of defining discrete energy-levels in the hydrogen atom. Being a partial differential equation, it offers a vast multitude of solutions, a multitude of even a higher transcendent order of magnitude than the system of solutions of the ordinary differential equations of ordinary mechanics. But the deficiency of the latter in atomic problems consisted, as is well known, by no means in that they supplied too small a number of possible orbits, but quite on the contrary, much too many. To select a discrete number of them as the "real" or "stationary" ones is, according to the view hitherto adopted, the task of the "quantum-conditions." Our wave equation (16), by augmenting the possibilities indefinitely, instead of restricting them, seems to lead us from bad to worse.

Happily because of the very interesting character which Eq. (16) takes in actual atomic problems, this fear proves to be erroneous. Putting for instance

$$V = -e^2/r, \tag{17}$$

(e = electronic charge, $r = (x^2+y^2+z^2)^{\frac{1}{2}}$, we get for the simplified hydrogen atom or one body problem:

$$\Delta\psi + 8\pi^2 m(E+e^2/r)\psi/h^2 = 0. \tag{18}$$

Now this equation for a great part of the possible values of the energy or frequency constant E, proves to offer no solution at all which is continuous, finite and single-valued throughout the whole space; for the E-values in question, every solution ψ, that satisfies the two other conditions (viz. continuity and single-valuedness) grows beyond all

limits either in approaching infinity or in approaching the origin of coordinates. The only E-values, for which this is not the case i.e. for which solutions exist, that are continuous, finite and single-valued throughout the whole space are the following ones

$$\begin{aligned} &(1) \qquad E>0 \\ &(2) \qquad E=-2\pi^2me^4/h^2n^2 \qquad (n=1,2,3,4\cdots) \end{aligned} \tag{19}$$

The first set corresponds to the hyperbolic orbits in ordinary mechanics. It is the general view, that according to ordinary quantum theory the hyperbolic orbits are not submitted to quantization. In our treatment this turns out quite spontaneously from the fact that every positive value of E leads to finite solutions. The second set corresponds exactly to Bohr's stationary energy levels of the elliptic orbits.

Though I cannot enter here upon the exact and rather tiresome proof of the foregoing statements, it may be interesting to describe in rough feature the solutions belonging to the second series of E-levels. The solution may be performed in three-dimensional[6] polar coordinates, by assuming ψ to be a product of a function of the polar angles and a function of the radius r only. The former is a spherical surface harmonic whose order, increased by unity, corresponds to the azimuthal quantum number. The functions of r, which come into play, somewhat resemble (in rough feature) the Bessel functions, though with the difference that they have but a finite number of positive roots, and this number exactly corresponds to the radial quantum number. These roots lie within a region from the origin of about the same order of magnitude as the corresponding Bohr orbit. After having passed the last root with increasing r and a maximum or minimum not far away from it, the function tends to diminish exponentially as r approaches infinity. So the whole of the wave-phenomenon, though mathematically spreading throughout all space, is essentially restricted to a small sphere of a few Angstroms diameter which may be called "the atom" according to undulatory mechanics. Any one of the above mentioned solutions (consisting of a product of a spherical surface-harmonic and a function of r only) greatly resembles a fundamental vibration of an elastic sphere, with a finite number of (1) spheres, (2) cones, (3) planes as "node surfaces." But it is surely not permissible to think that the wave-motion constituting the atom is, in general, restricted to one of these solutions, the special selection and separation of which is very much influenced by the choice

[6] It is of course not allowed to restrict the problem to two dimensions as in ordinary mechanics since the wave-phenomenon is essentially three-dimensional.

of coordinates. To every one of the discrete values of E belongs a finite number of special solutions. In forming a linear aggregate of them with arbitrary constant multipliers we get the most general solution of Eq. (18) for the particular value of E. The number of arbitrary constants entering into this aggregate is exactly equal to what is called the "statistical weight" of this energy-level, or in other words, to the number of separate levels into which it is split up according to Bohr's theory (and, by the way, also according to the present theory) by the addition of perturbing forces, that do away with the so-called "degeneration" of the problem. It will perhaps be remembered, that in ordinary quantum theory the number of states that is supplied by the method alluded to, is not exactly correct. Definite experimental evidence compels us to exclude by additional reasoning, more or less convincing from the theoretical point of view, a definite number of states, viz. those which have the equatorial quantum number zero. It is gratifying to be able to state, that according to the present theory the above mentioned number of arbitrary constants or, in other words, the number of separate levels or frequencies into which a degenerated E-level is split up by a perturbing potential is quite correct from the beginning. The theory needs no supplementation since it precludes a vibrational state corresponding to a Bohr-orbit with equatorial quantum number zero.

To complete this description we may add, that to the lowest E-level, or from the wave-motion point of view its "fundamental tone" which corresponds to the normal state of the atom, there belongs but one mode of vibration, and this is a very simple one; the function ψ shows complete spherical symmetry and there are no node surfaces at all. Both the radial quantum number as well as the order of the spherical surface harmonic vanish.

5. I should like to discuss in a few words the question, why Eq. (18) possesses finite solutions only for certain selected values of the constant E. The whole behavior described on the foregoing pages would be quite familiar to every physicist, if the problem were a so-called "boundary-condition problem," i.e. if the function ψ were required only in the interior of a given surface, let us say a sphere of given radius and had to fulfill certain conditions on the boundary of this sphere, e.g. to vanish. Now though this is not the case, the problem is indeed equivalent to a boundary-condition problem, the boundary being the infinite sphere. Thus the selected values (19) are quite properly to be named "characteristic values" and the solutions, that belong to them, "characteristic functions" of the problem connected with Eq. (18). The mathematical

reason,[7] why no boundary conditions in the proper sense of the word are neither needed nor allowed at the infinite boundary, is that a singular point of Eq. (18) is approached when we recede in any direction in space toward infinity. This can easily be seen by splitting up the equation in the way described above, using polar coordinates. The resulting ordinary differential equation with the variable r has two singularities, at $r=0$ and at $r=\infty$. It offers (for negative values of E) but one solution that remains finite at $r=0$, and but one that remains finite at $r=\infty$. These two solutions are in general not identical, but they are for the selected values of E given by (19).

But instead of dwelling on this purely mathematical side of the subject, I should like to present an idea why Eq. (18) shows such a queer behavior so as to make the matter clear to anyone who is acquainted only with the most general principles of wave theory. If E is negative, the bracket in Eq. (18) will be negative outside a certain sphere. Now remembering the way in which Eq. (18) was derived from Eq. (15), we see that a negative value of the bracket in (18) clearly means a negative value of the square of wave-velocity, or an imaginary value of wave-velocity. What does this imply? The Laplacian operator is well known to be intimately connected with the average excess of the neighboring values over the value of the function at the point considered. Thus the ordinary wave-equation (15) with a positive value of u^2 provides an accelerated increase (or a retarded decrease) of the function at all those points, where its value is lower than the average of the neighboring values; and, vice versa, a retarded increase (or an accelerated decrease) at those points where the function exceeds the average of its neighborhood. Thus the ordinary wave-equation represents a certain tendency to smooth out again all differences between the values of the function at different points, though not at the very moment they appear and not indefinitely—as in the case of the equation for heat conduction. It will however certainly prevent the function from increasing or decreasing beyond all limit.

If the quantity u^2, instead of being positive, is negative which we have seen to be sometimes the case with Eq. (18), then all the foregoing reasoning is just reversed. There is in the course of time a tendency to exaggerate infinitely all "humps" of the function and even spontaneously to form humps out of quite insignificant traces. Evidently a function which is subject to such a revolutionary sort of equation, is continually

[7] See e.g. R. Courant and D. Hilbert, Methoden der mathematischen Physik I (Berlin, Springer 1924), Chap. 5, §9, p. 1.

exposed to the very highest danger of increasing or decreasing beyond all limit. At any rate it is no longer astonishing, that special conditions must be fulfilled to prevent such an occurrence. The mathematical treatment shows that these conditions consist exactly in E having one of the second set of characteristic values given by (19), whereas the first set obviously prevents all accidents by making the square of the phase-velocity positive throughout the space.

6. I will now give an account of some of the results that have hitherto been obtained with this new mechanics. Rather simple problems are offered by the harmonic oscillator and the rotator. The E-levels of the former prove to be

$$(n+\tfrac{1}{2})h\nu_0\,; \qquad n=0,1,2,3\cdots$$

instead of $nh\nu_0$ according to the ordinary quantum theory. The E-levels of the rotator are

$$n(n+1)h^2/8\pi^2 I$$

(I = moment of inertia), the well known n^2 being replaced by $n(n+1)$. If we are interested only in the differences of levels—as is actually the case—this amounts to the same as replacing n^2 by $(n+\frac{1}{2})^2$, for

$$(n+\tfrac{1}{2})^2-n(n+1)=\tfrac{1}{4},$$

independent of n. It is well known that so-called half-quantum numbers are actually supported by the experimental evidence on most of the simple band spectra, and are probably contradicted by none of them. Mr. Fues, whose valuable help I owe to the Rockefeller Institution (International Education Board), has worked out[8] the band theory of diatomic molecules in detail, taking into account the mutual influence of rotation and oscillation and the fact, that the latter is not of the simple harmonic type. The result is in exact agreement with the ordinary treatment except that the quantum-numbers become half-integer also in all correction-terms. It would hardly have been possible to attack the problem just mentioned, as well as many similar ones, by direct methods, since the differential equation (16) is in general of a very difficult type. In many cases, however, this difficulty is overcome by the theory of perturbations which the writer has developed together with Mr. Fues. This theory, though much simpler, yet shows an interesting parallelism to the well known theory of perturbations in ordinary mechanics. It allows the calculation by mere quadratures of the small modification of characteristic values and characteristic functions, that are caused by

[8] E. Fues, Ann. d. Physik **80**, 367 (1926); another paper in press.

introducing an additional small term (function of the independent variables) in the coefficients of an equation whose characteristic values and characteristic functions are known.

An interesting example of the application of this mathematical theory is afforded by the perturbation of the hydrogen-atom caused by an external homogeneous electric field (Stark-effect). The discrete Balmer levels, shown in Eq.(19–2) are, as characteristic values, not simple but many fold. Each of them corresponds to n^2 characteristic values that coincide by chance or, more properly speaking, because of the high symmetry or simplicity of the coefficients of Eq. (18). The addition of an external electric field, small in comparison with the atomic field, does away with this symmetry and splits up every one of the Balmer-levels into a set of near neighboring levels, though not into as many as n^2, because the splitting up in this case is not thorough. The writer has been able to show that these levels exactly coincide with those given by the well known formula of Epstein, a rather severe test of our undulatory mechanics, since experimentally no deviation whatever, at least in the limit of a weak field, would have been allowed from this famous formula.

But not only the levels, i.e. the frequencies, but also the intensities and polarizations of the emitted lines in the Stark effect can be calculated from undulatory mechanics in very fair agreement with experiment. Hitherto we have not attached a definite physical meaning to the wave-function ψ. It is possible, however, to give it a certain electrodynamical meaning, which will be discussed in detail in Section 8 and which converts our atom into a system of fluctuating charges, spread out continuously in space and generating a resultant electric moment, that changes with time with a superposition of frequencies, which exactly coincide with the differences of the vibration-frequencies E/h, i.e. coincide with the frequencies of the emitted light. This in itself is highly satisfactory. But in addition it is possible to calculate the amplitudes of the harmonic components of the electric moment for any direction in space, e.g., in the case of the Stark effect, parallel to the electric field or perpendicular to the field. If the theory is correct, the squares of these amplitudes ought to be proportional to the intensities of the several line components, polarized in either direction. The rather laborious calculations have been performed and the result is shown in Fig. 1.[9] In comparing theory with experiment it must be born in mind that the calculations have been performed only in the limit of a very weak external

[9] The experimental data were taken from I. Stark, Ann. d. Physik **48**, 193 (1915). In these figures theoretical intensities that are too small to be indicated by a line of the proper length are marked by a dot.

field and that in the region of field-strength used in experiments (about 100,000 volts/cm) a very marked influence on the intensities is found both by experiment and by theory. In particular the very weak or vanishing components are enhanced with increasing field. The sum of the intensities of all the perpendicular components of one Balmer line turns out exactly equal to the sum of the parallel components of the same line. This is in full agreement with Stark's statement that no polarization of the emitted light as a whole is produced by the field.

I ought to emphasize here, that I was led to the foregoing nearly classical calculation of intensities by noticing *a posteriori*, i.e. after the main features of undulatory mechanics had been developed, its complete mathematical agreement with the theory of matrices put forward by Heisenberg, Born and Jordan.[10] The results shown in Fig. 1 may as well be called the results of the latter theory though they have not yet been calculated by its direct application. The connection of the two theories is a rather intricate one and is by no means to be observed at first sight.

7. It was stated in the beginning of this paper that in the present theory both the laws of motion and the quantum conditions can be deduced from one Hamiltonian principle. To prove this it must be shown that the wave-equation (16) can be derived from an integral-variation principle; for this equation is indeed the only fundamental equation of the theory (in the case of a single material point, moving in a conservative field of force, the only one considered in detail on the foregoing pages).

The connection of Eq. (16) with a Hamiltonian principle is very simple and almost exactly the same as in ordinary vibration problems. Furthermore this connection affords the simplest means of almost cogently extending the theory to a wholly arbitrary conservative system.

Suppose, the extreme values of the following integral extending over all space were required.

$$I_1=\int\int\int\{h^2[(\partial\psi/\partial x)^2+(\partial\psi/\partial y)^2+(\partial\psi/\partial z)^2]/8\pi^2m+V\psi^2\}\,dxdydz, \tag{20}$$

all single-valued, finite and continuously differentiable functions ψ being "admitted to concurrence" that give the following "normalizing" integral a constant value, say 1:

[10] W. Heisenberg, Zeits. f. Physik **33**, 879 (1925); M. Born and P. Jordan, ibid. **34**, 858 (1925); M. Born, P. Jordan and W. Heisenberg, ibid. **35**, 557 (1926); M. Born and N. Wiener, ibid. **36**, 174 (1926); W. Heisenberg and P. Jordan, ibid. **37**, 263 (1926); W. Pauli, Jr., ibid. **36**, 336 (1926); P. A. M. Dirac, Proc. Roy. Soc. **109**, 642 (1925); **110**, 561 (1925); **111**, 281, 405 (1926).

$$I_2=\int\int\int \psi^2 dxdydz=1 \tag{21}$$

In carrying out the variation under this "accessory condition" in the well known manner, Eq. (16) is found as the well known necessary condition for an extreme value of (20) the constant $-E$ being the Lagrangian multiplier with which the variation of the second integral has to be multiplied and added to the first, so as to take care of the accessory condition. Thus the normalized characteristic functions of Eq. (16) are exactly the so-called extremals of the integral (20) under the normalizing condition (21), whereas the characteristic values i.e. the values, that are admissible for the constant E are nothing else than the extreme values of integral (20). (This property of the Langrangian multiplier is well known and is easily recognized by observing, that the non-conditioned, extreme value of I_1-EI_2 can be but zero, any other value being capable as well of augmentation as of diminution by simply multiplying ψ by a constant.)

Now the integrand of (20) proves on closer inspection to have a very simple relation to the ordinary Hamiltonian function of our mechanical problem—in the sense of ordinary mechanics. The said function is, (cf. Section 1):

$$(1/2m)(p_x^2+p_y^2+p_z^2)+V(x,y,z). \tag{22}$$

Take this function to be a homogeneous quadratic function of the momenta p_x etc. and of unity and replace therein p_x, p_y, p_z, 1 by $(h/2\pi)$ $(\partial\psi/\partial x)$, $(h/2\pi)$ $(\partial\psi/\partial y)$, $(h/2\pi)$ $(\partial\psi/\partial z)$, ψ, respectively. There results the integrand of (20). This immediately suggests extending our variation problem and hereby our wave-equation (16) to a wholly arbitrary conservative mechanical system. The Hamiltonian function of such will be of the form

$$\tfrac{1}{2}\sum_{l=1}^{N}\sum_{k=1}^{N} a_{lk}p_lp_k+V \tag{23}$$

with $a_{lk}=a_{kl}$, the a_{lk} and V being some functions of the N generalized coordinates $q_1 \cdots q_N$. Take (23) to be a homogeneous quadratic function of $p_1 \cdots p_N$, 1 and replace these quantities by $(h/2\pi)$ $(\partial\psi/\partial q_1)$, $\cdots$ $(h/2\pi)$ $(\partial\psi/\partial q_N)$, ψ respectively. Writing Δ_p for the determinant

$$\Delta_p=\left|\sum \pm a_{ik}\right|$$

we form the integral

$$I_1=\int\cdots\int[(h^2/8\pi^2)\sum_l\sum_k a_{lk}(\partial\psi/\partial q_l)(\partial\psi/\partial q_k) +V\psi^2]\Delta_p^{-\frac{1}{2}}dq_1\cdots dq_N \tag{24}$$

taken over the whole space of coordinates and seek its extreme values under the accessory condition

$$I_2=\int\cdots\int\psi^2\Delta_p^{-1}dq_1\cdots dq_N=1 \tag{25}$$

This leads to the generalization of Eq. (16), viz.

$$\Delta_p^{\frac{1}{2}}\sum_l\frac{\partial}{\partial\dot{q}_l}\left(\Delta_p^{-\frac{1}{2}}\sum_k a_{lk}\partial\psi/\partial q_k\right)+(8\pi^2/h^2)(E-V)\psi=0, \tag{26}$$

$-E$ being, as before, the Lagrangian multiplier of (25). The double sum appearing in (26) is a sort of generalized Laplacian in the N-dimensional, non-euclidean space of coordinates. The necessary appearance of $\Delta_p^{-\frac{1}{2}}$ in an integral like (24) or (25) is well known from Gibbs' statistical mechanics; $\Delta_p^{-\frac{1}{2}}\,dq_1\cdots dq_N$ is simply the non-euclidean element of volume, e.g. $r^2\sin\theta d\theta d\phi dr$ in the case of one material point of unit mass, whose position is fixed by three polar coordinates r, θ, ϕ. (In omitting the determinant the integrals would not be invariant relative to point transformations; they would depend on the choice of generalized coordinates.) It is Eq. (26) that has been used in all problems mentioned in Section 6.

8. The question of the real physical meaning of the wave-function ψ has been delayed (see Section 6) until now for the sake of discussing it but once in full generality for a wholly arbitrary system. Eq. (16) or in the more general case, Eq. (26) gives the dependence of the wave-function ψ on the coordinates only, the dependence on time being given for every one particular solution, corresponding to a particular characteristic value $E=E_l$, by the real part of

$$\exp[(2\pi E_l t/h+\theta_l)i], \qquad i=\sqrt{-1}$$

the θ_l being phase constants. So if u_l ($l=1,\ 2,\ 3\cdots$) be the characteristic functions the most general solution of the wave-problem will be (the real part of)

$$\psi=\sum_{l=1}^{\infty}c_l u_l\exp[(2\pi E_l t/h+\theta_l)i]. \tag{27}$$

(For simplicity's sake we suppose the characteristic values to be all single and discrete.) The c_l are real constants. Now form the square of the absolute value of the complex function ψ. Denoting a conjugate complex value by a bar, this is

$$\psi\bar{\psi}=2\sum_{l,l'}c_l c_{l'}u_l u_{l'}\cos[2\pi(E_l-E_{l'})t/h+\theta_l-\theta_{l'}]. \tag{28}$$

This of course, like ψ itself, is in the general case a function of the generalized coordinates $q_1 \cdots q_N$ and the time,—not a function of ordinary space and time as in ordinary wave-problems. This raises some difficulty in attaching a physical meaning to the wave-function. In the case of the hydrogen atom (taken as a one-body problem) the difficulty disappears. In this case it has been possible to compute fairly correct values for the intensities e.g. of the Stark effect components (see Section 6, Fig. 1) by the following hypothesis: the charge of the electron is not concentrated in a point, but is spread out through the whole space, proportional to the quantity $\psi\bar{\psi}$.

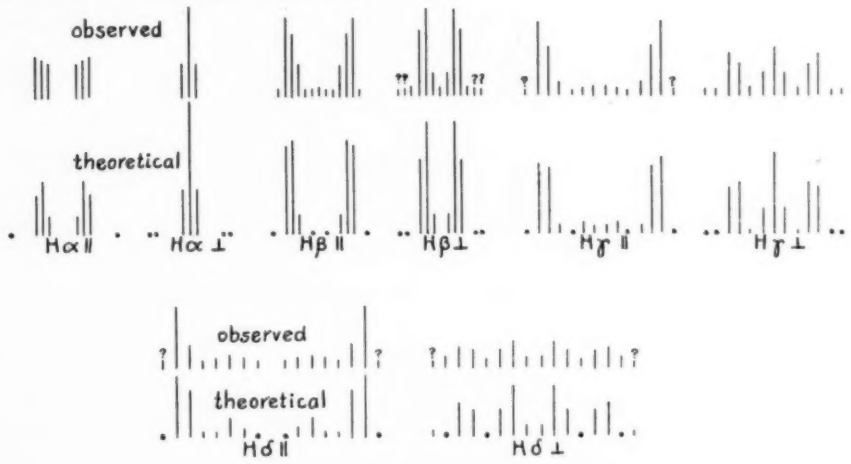

FIG. 1

It has to be born in mind, that by this hypothesis the charge is nevertheless restricted to a domain of, say, a few Angstroms, the wave-function ψ practically vanishing at greater distance from the nucleus (see Section 4). The fluctuation of the charge will be governed by Eq. (28), applied to the special case of the hydrogen atom. To find the radiation, that by ordinary electrodynamics will originate from these fluctuating charges, we have simply to calculate the rectangular components of the total electrical moment[11] by multiplying (28) by x, y, z respectively, and integrating over the space, e.g.[12]

$$\int\int\int z\psi\bar{\psi}dxdydz = 2\sum_{l,l'} c_l c_{l'} \cos\left[2\pi(E_l - E_{l'})t/h + \theta_l - \theta_{l'}\right]$$

[11] This procedure is legitimate only because and as long as the domain to which the charge is practically restricted remains small in comparison with the optical wave-length that corresponds to the frequencies $(E_l - E_{l'})/yh$.

[12] In the sum $\sum_{l,l'}$ each pair of values of l,l' is to be taken but once and the terms with $l' = l$ are to be halved.

$$\cdot \int\int\int z u_l u_{l'} dx dy dz \tag{29}$$

Thus the total electric moment is seen to be a superposition of dipoles, which are associated with the pairs of characteristic functions which vibrate harmonically with the frequencies $(E_l - E_{l'})/h$, well known from N. Bohr's famous frequency-condition. The intensity of emitted radiation of a particular frequency is to be expected proportional to the square of

$$c_l c_{l'} \int\int\int z u_l u_{l'} dx dy dz.$$

The supposition made on the c_l, in calculating the intensities of the Stark effect components, Fig. 1, is, that the c_l be equal for every set of characteristic values derived from one Balmer level (Eq. 19–2) by the action of the electrical field. The relative intensities of the fine structure components will then be proportional to the square of the triple integral. This is found to be in fair agreement with experiment.

The triple integral may be shown to be equal to what in Heisenberg's theory would be called the "element of matrix $z(l, l')$". This constitutes the intimate connection between the two theories. But the important achievement of the present theory—imperfect as it may in many respects be —seems to me to be that by a definite localization of the charge in space and time we are able from ordinary electrodynamics really to derive both the frequencies and the intensities and polarizations of the emitted light. All so-called selection principles automatically result from the vanishing of the triple integral in the particular case.

Now how are these conceptions to be generalized to the case of more than one, say of N, electrons? Here Heisenberg's formal theory has proved most valuable. It tells us though less by physical reasoning than by its compact formal structure that Eq. (29) giving a rectangular component of total electric moment has to be maintained with the only differences that (1) the integrals are $3N$-fold instead of three fold, extending over the whole coordinate space; (2) z has to be replaced by the sum $\sum e_i z_i$ i.e. by the z-component of the total electrical moment which the point-charge model would have in the configuration $(x_1, y_1, z_1; x_2, y_2, z_2; \cdots x_N, y_N, z_N)$ that relates to the element $dx_1 \cdots dz_N$ of the integration.

But this amounts to making the following hypothesis as to the physical meaning of ψ which of course reduces to our former hypothesis in the case of one electron only: the real continuous partition of the charge is a sort of mean of the continuous multitude of all possible configurations

of the corresponding point-charge model, the mean being taken with the quantity $\psi\psi$ as a sort of weight-function in the configuration space.

No very definite experimental results can be brought forward at present in favor of this generalized hypothesis. But some very general theoretical results on the quantity $\psi\bar{\psi}$ persuade me that the hypothesis is right. For example the value of the integral of $\psi\bar{\psi}$, taken over the whole coordinate space proves absolutely constant (as it should, if $\psi\bar{\psi}$ is a reasonable weight function) not only with a conservative, but also with a non-conservative system. The treatment of the latter will be roughly sketched in the following section.

9. Eq. (16) or more generally (26) which is fundamental to all our reasoning has been arrived at under the supposition that ψ depends on the time only through the factor

$$e^{\pm 2\pi i E t/h} \tag{30}$$

But this amounts to saying, that

$$\dot{\psi} = \pm 2\pi i E\psi/h. \tag{31}$$

From this equation and from Eq. (26) the quantity E may be eliminated and so an equation be formed that must hold in any case, whatever be the dependence of the wave-function ψ on time:

$$\Delta_p^{\frac{1}{2}} \sum_l \frac{\partial}{\partial q_l}\left(\Delta_p^{-\frac{1}{2}} \sum_k a_{lk}\partial\psi/\partial q_k\right) - 8\pi^2 V\psi/h^2 \mp (4\pi i/h)\partial\psi/\partial t = 0 \tag{32}$$

The ambiguous sign of the last term presents no grave difficulty. Since physical meaning is attached to the product $\psi\bar{\psi}$ only, we may postulate for ψ either of the two equations (32); then $\bar{\psi}$ will satisfy the other and their product will remain unaltered.

Eq. (32) lends itself to generalization to an arbitrary non-conservative system by simply supposing the potential function V to contain the time explicitly. A case of greatest interest is obtained by adding to the potential energy of a conservative system a small term; viz., the non-conservative potential energy, produced in the system by an incident light wave. We cannot enter here into the details, but shall only present the main features of the solution. The effect of the incident light wave is, that with each free vibration of the undisturbed system, frequency E_l/h, there are associated two forced vibrations with, in general, very small amplitudes and with the two frequencies $E_l/h \pm \nu$, ν being the frequency of the incident beam of light. Following the same principles as in the foregoing section we find every free vibration, cooperating with

its associated forced vibrations to give rise to a forced light emission with the difference frequency

$$E_l/h-(E_l/h\pm\nu)=\mp\nu$$

i.e. with exactly the frequency of the incident beam of light. This forced emission is of course to be identified with the secondary wavelets that are necessary to account for absorption, dispersion and scattering. In calculating their amplitudes one finds them, indeed, to increase very markedly as soon as the incident frequency ν approaches any one of the emission frequencies $(E_l-E_{l'})/h$. The final formula is almost identical with the well known Helmholtz dispersion formula in the form presented by Kramers.[13]

The case of resonance cannot yet be treated quite satisfactorily, since a damping-term seems to be missing in our fundamental equation, even in the case of a free conservative system. (The radiation, which according to the assumptions of Section 8 is emitted by the cooperation of every pair of free vibrations, must of course in some way alter their amplitudes. This it does not do according to the assumptions hitherto made.) But it is quite interesting to observe that also with that damping term still missing, we do not encounter the accident of infinite amplitudes in the case of resonance, well known from the classical treatment of the subject. The only thing that happens is that an incident light wave of ever so small an amplitude will raise the forced vibration of the system to a finite amplitude. And furthermore if, for example, from the beginning only one free vibration was set up, say that belonging to $E_{l'}$ and if

$$h\nu=E_{l'}-E_l,$$

then the forced vibration, raised to finite amplitude, is in shape and frequency identical with the free vibration belonging to $E_{l'}$. At the same time the amplitude of the vibration E_l is markedly diminished. The sum of squares of all amplitudes remains constant under all circumstances. This behavior seems to afford an insight (though incomplete) into the so-called transition from one stationary state to another which hitherto has been wholly inaccessible to computation.

10. In the foregoing report the undulatory theory of mechanics has been developed without reference to two very important things, viz. (1) the relativity modifications of classical mechanics, (2) the action of a magnetic field on the atom. This may be thought rather peculiar since L. de Broglie, whose fundamental researches gave origin to the present

[13] H. A. Kramers, Nature, May 10 (1924), Aug. 30 (1924); H. A. Kramers and W. Heisenberg, Zeits. f. Physik **31**, 681 (1925).

theory, even started from the relativistic theory of electronic motion and from the beginning took into account a magnetic field as well as an electric one.

It is of course possible to take the same starting point also for the present theory and to carry it on fairly far in using relativistic mechanics instead of classical and including the action of a magnetic field. Some very interesting results are obtained in this way on the wave-length displacement, intensity and polarization of the fine structure components and of the Zeeman components of the hydrogen atom.[14] There are two reasons why I did not think it very important to enter here into this form of the theory. First, it has until now not been possible to extend the relativistic theory to a system of more than one electron. But there is the region in which the solution of new problems is to be hoped from the new theory, problems that were inaccessible to the older theory.

Second, the relativistic theory of the hydrogen atom is apparently incomplete; the results are in grave contradiction with experiment, since in Sommerfeld's well known formula for the displacement of the natural fine structure components the so-called azimuthal quantum number (as well as the radial quantum number) turns out as "half-integer," i.e. half of an odd number, instead of integer. So the fine structure turns out entirely wrong.

The deficiency must be intimately connected with Uhlenbeck-Goudsmit's[15] theory of the spinning electron. But in what way the electron spin has to be taken into account in the present theory is yet unknown.

ZÜRICH, SWITZERLAND,
September 3, 1926.

[14] V. Fock, Zeits. f. Physik **38**, 242 (1926).
[15] G. E. Uhlenbeck and S. Goudsmit, Physica (1925); Nature, Feb. 20 (1926).

NATURAL IONIZATION IN SPHERICAL CONTAINERS; THEORETICAL CONSIDERATIONS

By James W. Broxon

Abstract

Theory of the variations with pressure and size of container of the natural ionization in gases in spherical containers.—The variations with pressure and size of container of the natural ionization in gases in spherical containers are explained in terms of simple radiations. These radiations differ chiefly with regard to their origin and range. Radiations with equal propagation in all directions, uniform ionization along a path, and with ranges either greater or less than the diameter of the sphere, are considered with origin either throughout the volume or at the inner surface of the container. Radiations are also considered with origin at the inner surface of the sphere, direction normal to the surface, and absorption exponential with the distance traversed. The observed pressure variation of the natural ionization in air is given accurately by the formulas derived, upon assuming the ionization to be due entirely to the secondary and tertiary radiations excited in the gas and its container by a primary penetrating radiation. The volume variation is given qualitatively but not quantitatively in this instance, and the constants are interpreted. The pressure variation in the case of carbon dioxide is also closely approximated.

Introduction

In a recent experimental investigation,[1] it was found by the writer that the natural ionization in gases in closed spherical vessels increased with the pressure to 70 or 75 atmospheres, but that the pressure rate of increase became very small at high pressures. With certain gases, pressure-ionization curves became practically straight lines at high pressures, while with others the curvature persisted throughout. Measurements made with spheres of different sizes showed that at pressures above a few atmospheres the ionization did not vary unidirectionally with the size of the container, but passed through a minimum.

In view of the facts mentioned above, it was thought worth while to determine as a function of the size of the container and the pressure of the gas, the ionization which would be produced in a gas in a spherical container by a few very simple radiations.

Rays with Origin Throughout Volume

Rays of Range $C \geqq 2a$. Entirely for facility of mathematical derivation, we shall separately consider radiations of certain restricted ranges.

[1] J. W. Broxon, Phys. Rev. **27**, 542 (1926).

Therefore, we shall first consider the ionization due to rays of very long range which may be supposed to travel in straight lines until they reach the walls of the container, whatever be the pressure, i.e., rays of range $\geqq 2a$, where a is the radius of the spherical ionization chamber. We shall assume that the ionization per cm of path of these rays is constant (for a fixed pressure), and that the rays are emitted uniformly in all directions from their sources. If we imagine such rays to originate in a uniform manner throughout the volume of the container, then if $4\pi\gamma_c$ is the number of rays emitted per sec. from unit volume, $\gamma_c d\tau$ is the number of rays emitted per sec. in unit solid angle from the volume element, $d\tau$.

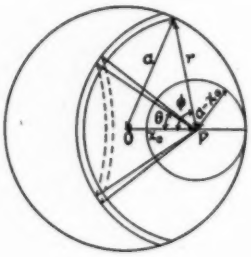

Fig. 1.

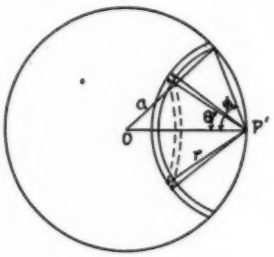

Fig. 2.

If C_c be the number of ions produced per cm of path by one "ray," $\gamma_c C_c d\tau d\Omega ds$ represents the number of ions produced per sec. along the element, ds, of their path by the rays emitted within the solid angle, $d\Omega$, from the volume element, $d\tau$.

Let us now proceed to determine N_c', the total number of ions produced per sec. within the spherical chamber by the rays emitted from a particular volume element, $d\tau$, situated at P (Fig. 1), distant x_o from O, the center of the chamber.

The number of ions produced per sec. inside a sphere of radius $(a-x_o)$ with center at P, is seen to be

$$N_{c1}' = 4\pi\gamma_c C_c d\tau (a-x_0).$$

To find N_{c2}', the number of ions produced per sec. outside this sphere but within the chamber, let us note that the number produced per sec. in the region between the two spherical surfaces with centers at P and of radii r and $(r+dr)$, cut off by all radii of the latter which make angles θ or $(\theta+d\theta)$ with OP, is

$$dN_{c2}' = \gamma_c C_c d\tau d\Omega ds = \gamma_c C_c d\tau \frac{2\pi r^2 \sin\theta d\theta}{r^2} dr.$$

Therefore,

$$N_{c2}' = 2\pi\gamma_c C_c d\tau \int_{r=a-x_0}^{r=a+x_0} \int_{\theta=0}^{\theta=\phi} \sin\theta d\theta dr, \text{ where } \cos\phi = \frac{x_0^2+r^2-a^2}{2x_0 r}$$

$$= \pi\gamma_c C_c d\tau \left[\frac{(a^2-x_0^2)}{x_0} \log \frac{a+x_0}{a-x_0} + 4x_0 - 2a \right]$$

$$N_c' = N_{c1}' + N_{c2}' = \pi\gamma_c C_c \left[\frac{(a^2-x_0^2)}{x_0} \log \frac{a+x_0}{a-x_0} + 2a \right] d\tau$$

The first term in the above bracket approaches 0 as $x_o \to a$, and $2a$ as $x_o \to 0$. We are therefore justified in using the value found for N_c' in calculating N_c, the total number of ions produced per sec. by all the rays of range $\geqq 2a$ produced throughout the volume of the sphere.

We have assumed that the rays originate uniformly throughout the chamber, which is the equivalent of assuming that γ_c is the same for all volume elements. We shall also consider C_c to be the same for rays from all volume elements. Therefore, the number of ions produced within the ionization chamber by rays emitted from the region between spherical surfaces of radii r_o and (r_o+dr_o) with centers at O, is given by

$$dN_c = \pi\gamma_c C_c \left[\frac{(a^2-r_0^2)}{r_0} \log \frac{a+r_0}{a-r_0} + 2a \right] 4\pi r_0^2 dr_0.$$

Therefore,

$$\frac{N_c}{4\pi^2\gamma_c C_c} = \int_{r_0=0}^{r_0=a} \left[(a^2 r_0 - r_0^3) \log \frac{a+r_0}{a-r_0} + 2ar_0^2 \right] dr_0 = a^4,$$

as is seen after proper evaluation of the first term. Hence $N_c = 4\pi^2\gamma_c C_c a^4$. The number of ions per cc per sec. produced by rays of this range originating throughout the volume of the sphere is therefore given by

$$n_c = \pi\gamma_c C_c (3a).$$

Rays of Range B, where $a \leqq B \leqq 2a$. We shall now proceed to find expressions similar to the preceding, for ionization due to radiations resembling the ones first discussed but of definite range of a magnitude between that of the radius and the diameter of the sphere. Let us note that the longest path of the radiations from any volume element at a distance x_o from the center of the chamber is B, providing $B \leqq (a+x_o)$, or $x_o \geqq (B-a)$; whereas the longest path is $(a+x_o)$, in case $B \geqq (a+x_o)$, or $x_o \leqq (B-a)$.

The number of ions produced per sec. by rays originating in a certain volume element, $d\tau$, situated inside a spherical surface concentric with the chamber wall and of radius, $(B-a)$, is therefore

$$N_B' = 4\pi\gamma_B C_B(a-x_0)d\tau + 2\pi\gamma_B C_B d\tau \int_{r=a-x_0}^{r=a+x_0} \int_{\theta=0}^{\theta=\phi} \sin\theta d\theta dr, \text{ where } \cos\phi = \frac{x_0^2+r^2-a^2}{2x_0 r}$$

$$= \pi\gamma_B C_B d\tau \left[\frac{(a^2-x_0^2)}{x_0}\log\frac{a+x_0}{a-x_0} + 2a\right] = dN_{B1},$$

where γ_B and C_B correspond to γ_c and C_c, respectively, and where N_{B1} represents the total number of ions produced per sec. by rays originating within the sphere of radius $(B-a)$ concentric with the chamber wall. Then

$$N_{B1} = \pi\gamma_B C_B \int_{r_0=0}^{r_0=B-a} \left[\frac{(a^2-r_0^2)}{r_0}\log\frac{a+r_0}{a-r_0} + 2a\right] 4\pi r_0^2 dr_0$$

$$= 4\pi^2\gamma_B C_B \left[\frac{(a^2-r_0^2)^2}{4}\log\frac{a-r_0}{a+r_0} + \tfrac{1}{2}(a^3 r_0 + a r_0^3)\right]_{r_0=0}^{r_0=B-a}.$$

The number of ions produced per sec. by rays originating in a volume element situated without the designated spherical surface of radius $(B-a)$ but within the chamber, is given by

$$N_{B2}' = 4\pi\gamma_B C_B(a-x_0)d\tau + 2\pi\gamma_B C_B d\tau \int_{r=a-x_0}^{r=B} \int_{\theta=0}^{\theta=\phi} \sin\theta d\theta dr$$

$$= \pi\gamma_B C_B d\tau \left[\frac{(a^2-x_0^2)}{x_0}\log\frac{B}{a-x_0} + \frac{a^2-B^2}{2x_0} - 3x_0/2 + 2B + a\right] = dN_{B2},$$

where N_{B2} represents the total number of ions per sec. due to rays originating in the entire region within the chamber and outside the surface of radius $(B-a)$. Therefore,

$$N_{B2} = \int_{r_0=B-a}^{r_0=a} dN_{B2} = 4\pi^2\gamma_B C_B \left[\left(B^3 a - B^2 a^2 - \frac{1}{4}B^4\right)\log(2a-B) + \left(\frac{1}{4}B^4 + B^2 a^2 - B^3 a\right)\log B + a^4 - \frac{2}{3}Ba^3 + B^2 a^2 - \frac{1}{2}B^3 a + \frac{B^4}{48}\right].$$

The total number of ions per sec. produced by rays of range B originating throughout the volume of the chamber in the manner described, is

$$N_B = N_{B1} + N_{B2} = \pi^2 \gamma_B C_B \left[\frac{16}{3} B a^3 - 2B^2 a^2 + \frac{1}{12} B^4 \right].$$

Therefore, the number of ions per cc per sec. due to these rays is

$$n_B = \pi \gamma_B C_B \left[4B - \frac{3}{2} B^2 a^{-1} + \frac{1}{16} B^4 a^{-3} \right]$$

Rays of Range A, where $0 \leqq A \leqq a$. To find expressions similar to the preceding, for ionization due to similar rays of range not greater than the radius of the chamber, let us note that all such rays which originate within a sphere concentric with the container and of radius $(a-A)$, will complete their range. Hence the number of ions produced per sec. by rays of range A from a volume element within this region is $N_{A1}' = 4\pi\gamma_A C_A A d\tau$, and the total number of ions produced per sec. by rays originating inside this sphere is $N_{A1} = 4\pi\gamma_A C_A A \cdot \frac{4}{3}\pi(a-A)^3$, where γ_A and C_A correspond to previous similar symbols.

Let us next determine the number of ions produced per sec. by rays originating in the region outside the designated sphere of radius $(a-A)$. The number of ions produced per sec. by rays originating in a volume element, $d\tau$, in this region at a distance, x_0, from O, where $(a-A) < x_0 \leqq a$, is

$$N_{A2}' = 4\pi\gamma_A C_A (a - x_0) d\tau + 2\pi\gamma_A C_A d\tau \int_{r=a-x_0}^{r=A} \int_{\theta=0}^{\theta=\phi} \sin\theta d\theta dr, \text{ where } \cos\phi = \frac{x_0^2 + r^2 - a^2}{2x_0 r}$$

$$= \pi\gamma_A C_A d\tau \left[\frac{(a^2 - x_0^2)}{x_0} \log \frac{A}{a - x_0} + \frac{a^2 - A^2}{2x_0} - 3x_0/2 + 2A + a \right] = dN_{A2},$$

where N_{A2} represents the number of ions per sec. due to all rays of Range A originating outside the sphere of radius, $(a-A)$. Therefore,

$$N_{A2} = \pi\gamma_A C_A \int_{r_0=a-A}^{r_0=a} \left[\frac{(r_0 - a^2)}{r_0} \log \frac{a - r_0}{A} + \frac{a^2 - A^2}{2r_0} - 3r_0/2 + 2A + a \right] 4\pi r_0^2 dr_0$$

$$= 4\pi^2 \gamma_A C_A \left[7A^2 a^2/2 - 4A^3 a + \frac{65}{48} A^4 \right]$$

The number of ions per sec. due to all such rays originating throughout the spherical container is therefore

$$N_A = N_{A1} + N_{A2} = \pi^2 \gamma_A C_A [16 A a^3/3 - 2A^2 a^2 + A^4/12]$$

and the number of ions per cc per sec. due to these rays is

$$n_A = \pi\gamma_A C_A [4A - 3A^2 a^{-1}/2 + A^4 a^{-3}/16]$$

Rays with Origin at Surface of Container

Rays of Range $C \geqq 2a$. Let us next consider the effect due to rays of the same range and ionizing ability as those first considered, but which are supposed to originate uniformly over the interior surface of the chamber and to be emitted radially and uniformly in all directions from their sources. If $4\pi\gamma_c'$ represent the total number of rays of this range (effective and otherwise) which originate from unit area of the surface, and C_c', the number of ions produced per cm of path by one of these rays, then the number of ions produced per sec. along the element, ds, of their path by the rays emitted within the solid angle, $d\Omega$, from the surface element, dS, is $\gamma_c' C_c' dS d\Omega ds$, providing $d\Omega$ and ds be within the chamber.

The total number of ions produced per sec. within the spherical chamber by the rays emitted from a particular element, dS, situated at P' (Fig. 2), is

$$N_c'' = 2\pi\gamma_c' C_c' dS \int_{r=0}^{r=2a} \int_{\theta=0}^{\theta=\phi} \sin\theta d\theta dr, \text{ where } \cos\phi = r/2a$$

$$= 2\pi\gamma_c' C_c' a dS.$$

The total number of ions produced within the chamber in one second by rays of this type emitted from the entire surface is therefore $N_c''' = 8\pi^2\gamma_c' C_c' a^3$, and the number of ions per cc per sec. produced by these rays is $n_c' = 6\pi\gamma_c' C_c'$.

Rays of Range B, *where* $a \leqq B \leqq 2a$. Let γ_B' correspond to γ_c', and C_B' to C_c', and as in the case of the long range radiations, let us proceed to find a value for n_B', corresponding to n_c'. The number of ions produced per sec. by rays from an element of area, dS, is given by

$$N_B'' = 2\pi\gamma_B' C_B' dS \int_{r=0}^{r=B} \int_{\theta=0}^{\theta=\phi} \sin\theta d\theta dr, \text{ where } \cos\phi = r/2a$$

$$= 2\pi\gamma_B' C_B' (B - B^2/4a) dS.$$

The number of ions produced per sec. by the radiation from the entire surface is therefore $N_B''' = 8\pi^2\gamma_B' C_B' (Ba^2 - B^2a/4)$ and the number of ions per cc per sec. due to these rays is

$$n_B' = 6\pi\gamma_B' C_B' (Ba^{-1} - \tfrac{1}{4}B^2a^{-2}).$$

Rays of Range A, *where* $0 \leqq A \leqq a$. Exactly as in the case of rays of range B, the number of ions per cc per sec. due to rays of range A, originating at the inner surface of the container is found to be $n_A' = 6\pi\gamma_A' C_A' (Aa^{-1} - \tfrac{1}{4}A^2a^{-2})$.

It will be noticed that the expressions found for "n" and "n'" exactly correspond in the two cases of ionization due to radiations of definite range less than the diameter of the ionization chamber. The only reason for considering the two sets of ranges separately was to facilitate the choosing of the proper definite limits of integration. We may therefore sum up these two cases by noticing that if $0 \leqq D \leqq 2a$, the number of ions per cc per sec. produced by radiations of range D originating uniformly throughout the volume, proceeding uniformly in all directions from the volume elements in which they originate, and ionizing uniformly along their paths, is given by

$$n_D = \pi \gamma_D C_D (4D - 3D^2 a^{-1}/2 + D^4 a^{-3}/16).$$

The number of ions per cc per sec. produced by such rays originating uniformly at the inner surface of the container is

$$n_D' = 6\pi \gamma_D' C_D' (Da^{-1} - D^2 a^{-2}/4).$$

Rays of Exponentially Decreasing Ionizing Ability

Proceeding as does W. Wilson,[2] we may derive an expression for the ionization which would result from a radiation given off normally and uniformly from the interior surface of the container and being absorbed according to an exponential law with the distance traversed.

If dI' represents the number of ions per sec. produced in a layer of thickness dx at a normal distance x, by the rays originating on an element of area, dS, of the inner surface of the sphere, the total number of ions produced per sec. within the spherical chamber by the radiation from this element is given by

$$I' = \int dI' = \int_{x=0}^{x=2a} I_0 e^{-\lambda' x} dx dS = \frac{I_0}{\lambda'}(1 - e^{-2a\lambda'}) dS.$$

Then the total ions per sec. due to the rays from the entire surface is

$$N_F = \frac{4\pi I_0}{\lambda'} a^2 (1 - e^{-2a\lambda'})$$

and the number of ions per cc per sec.,

$$n_F = 3\frac{I_0}{\lambda'} a^{-1} (1 - e^{-2a\lambda'}).$$

Assuming $I_0 \propto \lambda' \propto P$, we may write

$$n_F = Ba^{-1}(1 - e^{-2\lambda aP}),$$

[2] W. Wilson, Phil. Mag. **6**, 216 (1909).

where B is a constant, P the pressure (in atmospheres) and λ the coefficient of absorption at atmospheric pressure.

In the above, no account has been taken of the possibility of the emission of the radiations in various directions or of their production within the metal beneath the inner surface of the container. The method of procedure in that case, as well as a certain justification for not considering the case here, may be found in a paper by Campbell.[3]

Dependence upon Pressure

The ionization formulas derived are collected in the following table:

Radiation Number.	*Origin.*	*Range.*	*Ions per cc per sec.*
C	throughout volume	$\geqq 2a$	$n_c = \pi\gamma_c C_c(3a)$.
D	throughout volume	$\leqq 2a$	$n_D = \pi\gamma_D C_D(4D - 3D^2a^{-1}/2 + D^4a^{-3}/16)$.
C'	at surface	$\geqq 2a$	$n_c' = 6\pi\gamma_c' C_c'$.
D'	at surface	$\leqq 2a$	$n_D' = 6\pi\gamma_D' C_D'(Da^{-1} - D^2a^{-2}/4)$.
F	at surface	—	$n_F = Ba^{-1}(1 - e^{-2\lambda aP})$

The above expressions show how the ionization would depend upon the radius of the container if it were due to any of the radiations considered, and the dependence upon the pressure also is shown in the case of n_F. It is now desired to arrive at a conclusion as to how the remaining expressions may be expected to depend upon the pressure. With this in view, the following suggestions as to the possible causes of the radiations are made: (1) a very penetrating radiation from a considerable distance; (2) spontaneous ionization of the gas; (3) a radioactive substance admitted with the gas; (4) chemical action between the gas and the walls of the container; (5) chemical action between two component gases; (6) radioactive contamination of the walls of the container; (7) disintegration of the walls of the container. Other possibilities readily suggest themselves, of course, but it is desired to restrict attention to a few simple ones.

Resulting γ's would probably be proportional to P if the ionization were due to causes (1), (2) or (3), and to P^2 if due to (5). If the ionization were due to (4), the resulting γ' would probably be proportional to P, while constant γ''s would be expected to result from (1), (6) or (7).

In all cases of uniform ionization along the paths of the rays, it seems reasonable to suppose that the ions per cm of path (the C's) would be

[3] N. R. Campbell, Phil. Mag. 9, 531 (1905).

proportional to the pressure, and that the ranges would be inversely proportional to the pressure. We therefore might have any $\gamma \propto P$, or $\propto P^2$; $\gamma' \propto P$, or constant; $C \propto C' \propto P$; $D \propto 1/P$. The corresponding expressions for n would then become:

$$n_c = K_1 P^2 a \quad , \text{ or } \quad n_c = K_2 P^3 a \quad ;$$

$$n_D = K_3 P - K_4 a^{-1} + K_5 P^{-2} a^{-3} , \text{ or } \quad n_D = K_6 P^2 - K_7 a^{-1} P + K_8 P^{-1} a^{-3} ;$$

$$n_c' = K_9 P \quad , \text{ or } \quad n_c' = K_{10} P^2 \quad ;$$

$$n_D' = K_{11} a^{-1} - K_{12} P^{-1} a^{-2} \quad , \text{ or } \quad n_D' = K_{13} P a^{-1} - K_{14} a^{-2} \quad ;$$

where the K's are constants.

Primary effects due to (1), (2), (3) and (4), apart from resulting radiations, would probably result in ions per cc per sec. proportional to the pressure at constant volume, and independent of changes in volume at constant pressure. Due to a similar primary effect of (5), the ions per cc per sec. might be proportional to the square of the pressure for constant volume, and vary directly with the volume at constant pressure.

Application to Experimental Observations

Let us now attempt by means of the formulas we have derived, to approximate the variation of the natural ionization with volume of chamber and pressure of gas as already determined experimentally.[1]

As a specific example, let us consider the ionization in air in the 9-inch sphere. Suppose this ionization is due entirely to a very hard radiation, the primary effect of which is negligible in comparison to its secondary and tertiary effects, so far as its contribution to the total ionization is concerned. Let us further suppose that the electrons ejected by the penetrating radiation from the gas itself have very long ranges (C-number), and that these in turn produce tertiary rays of short range (D-number); and that those electrons ejected by the penetrating radiation at the surface of the container are of two sorts, one emitted normally and being absorbed exponentially along its path (F-number), and the other being emitted diffusely and ionizing uniformly along its path which we shall consider to be 24 ft. in air at atmospheric pressure. This last radiation would then be termed C'-number at pressures below 32 atmospheres and D'-number at pressures above 32 atmospheres.

Apparently n_P and hence B must be proportional to S, the intensity of the primary penetrating radiation.

Let us suppose that the number of long-range or C-number rays produced per sec. is proportional to S, but not to the pressure, P, being independent of the latter. This might be the situation if they arose

almost entirely from certain nuclei (as unremoved dust particles) distributed throughout the volume of the sphere, no new nuclei being admitted with additional gas. Thus we may assume $\gamma_c \propto S$ and $C_c \propto P$.

If the D-number rays are almost entirely of tertiary origin, we might expect their rate of production to be proportional to n_c and also to the pressure. It might conceivably be, however, although we are postulating that the C-number rays ionize uniformly along their paths, that the fraction of its ions which result in D-number rays decreases in some manner with the distance from its origin along the path of a C-number ray. The effective paths of the latter increase, in general, with the size of the sphere. We shall therefore assume that $\gamma_D \propto Pn_c/a$ and for the D-number rays, $D \propto 1/P$ and $C_D \propto P$.

Concerning the D'-number rays we shall simply assume $\gamma_D' \propto S$ and independent of P, $C_D' \propto P$, and $D \propto 1/P$.

Since the D'-number rays become C'-number rays at pressures below 32 atmospheres, we must likewise have $\gamma_c' = \gamma_D'$ and $C_c' = C_D'$.

In accordance with the foregoing hypotheses, we may now write our ionization formulas in the forms:

(1) $n_F = Ba^{-1}(1-e^{-2\lambda aP})$, (2) $n_c = G_1 aP$,

(3) $n_D = G_2P^2 - G_3a^{-1}P + G_4a^{-3}P^{-1}$, (4) $n_D' = G_5a^{-1} - G_6a^{-2}P^{-1}$,

(5) $n_c' = G_7P$,

where

(6) $G_1 = 3\pi K_2K_3S$, (7) $G_2 = 4\pi G_1K_4K_5K_6$,

(8) $G_3 = 3\pi G_1K_4K_5K_6^2/2$, (9) $G_4 = \pi G_1K_4K_5K_6^4/16$,

(10) $G_5 = 6\pi K_7K_8K_9S$, (11) $G_6 = 3\pi K_7K_8K_9^2S/2$,

(12) $G_7 = 6\pi K_7K_8S$,

where

(13) S represents intensity of the primary penetrating radiation.

(14) λ is coeff. of absorption of F-number rays in air at atm. press.

(15) $B(1-e^{-2\lambda})/S$ gives the ionization due to F-number rays per unit intensity of the primary radiation in air at atm. press. in a sphere of unit radius.

(16) $4\pi K_2$ is no. of C-number rays per unit vol. per sec. per unit S.

(17) $4\pi K_7$ is no. of C'- or D'-number rays per unit area per sec. per unit S.

(18) $4\pi K_4$ is no. of D-number rays per unit vol. per ion of the C-number at atm. press. in a sphere of unit radius.

(19) K_3 is no. of ions produced by a C-number ray per cm path at atm. press.

(20) K_5 is no. of ions produced by a D-number ray per cm path at atm. press.

(21) K_8 is no. of ions produced by a C'- or D'-number ray per cm path at atm. press.

(22) K_6 is range of D-number rays in air at atmospheric pressure.

(23) K_9 is range of D'-number rays in air at atmospheric pressure.

In Eqs. (1)–(5), let us put $\lambda=.081$; $B=34.0$; $G_1=.552-$; $G_2=.0001$; $G_3=.458$; $G_4=7.0$; $G_5=66.7$; $G_6=1057.8$; $G_7=1.066$. We have then

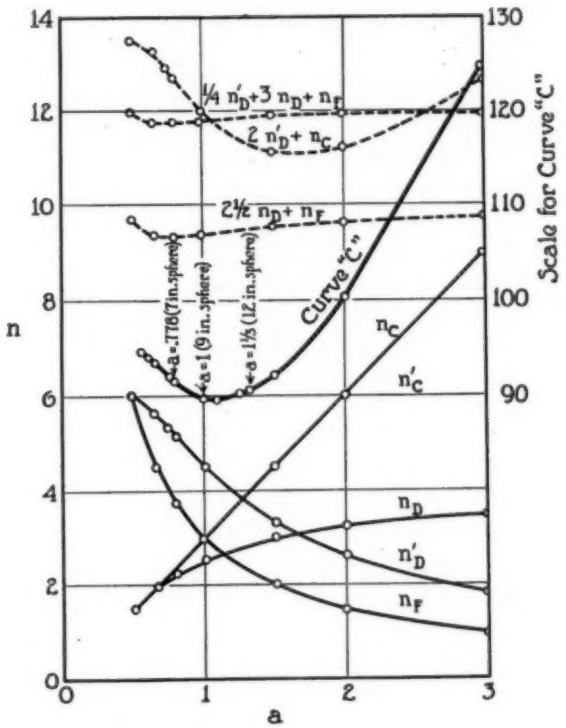

Fig. 3. In these curves (excepting curve C): $\pi\gamma_D C_D=\pi\gamma_C C_C=\pi\gamma'_D C'_D=\pi\gamma'_C C'_C=I=D$; $B=3$; $2\lambda P=10$.

as our pressure-ionization formulas (approximately):
(for $1\leqq P\leqq 32$)

$$n=n_F+n_c'+n_c+n_D=34(1-e^{-.162P})+1.16P+7P^{-1}+.0001P^2, \quad (24)$$

(for $P>32$)

$$n=n_F+n_D'+n_c+n_D=34(1-e^{-.162P})+\frac{3}{32}P$$
$$+.0001P^2+66.7-1050.8P^{-1}, \quad (25)$$

where the radius, a, has been chosen as unity. With the same values of

the above λ, B, G's, we have as the relation between the ionization and the radius of the chamber at a pressure of 61.73 atmospheres, the approximate equation

$$n = n_F + n_D' + n_c + n_D = 34a^{-1}(1-e^{-10a}) + 38.43a^{-1} + 34a - 17.136a^{-2} + .38 + .113a^{-3}. \quad (26)$$

In Fig. 4 (Air—9-in. S.) n as given by Eqs. (24) and (25) has been plotted as a function of P. It is seen that the observed pressure variation is very closely approximated.

In Fig. 3 (Curve C) n as given by Eq. (26) is plotted as a function of a. An inspection of this curve shows that by using the same constants (G's, etc.) as in the $n-P$ formulas, we were able to predict that the ionization at a given high pressure would pass through a minimum as the radius of the sphere was varied, and in fact this minimum is so situated that we should have less ionization in the 9-inch sphere than in either the 7-inch or the 12-inch sphere. Also, this difference is greater at higher pressures. However, this agreement is not quantitative, as the observed ionizations in the 7-inch and 12-inch spheres were much greater than our formula indicates. Thus according to Fig. 3 we should have $n=91.97$, 89.78, and 90.44 for the 7-, 9-, and 12-inch spheres respectively. The observed values, however, were approximately 100.0, 89.8 and 126.0— in the three cases, respectively. The difference here mentioned is so large that we must consider our n-a formulas quantitatively inadequate in spite of the fact that observations were taken with only three different spheres. It is possible that there were other variables such as the condition of the surfaces of the particular spheres used, which served to accentuate the variation in this instance. The matter could be determined definitely, of course, only by making observations with a considerable number of spheres of various sizes, care being taken that they should be very similar in all other respects. In this regard it is worth noting that the volume variations were much smaller when the spheres were lined with aluminum, although the ionization was still least in the 9-inch sphere.

Let us now turn to an inspection of our constants and their interpretation in terms of the fundamental phenomena. We have already assigned the value 0.081 to λ which gives the coefficient of absorption of the F-number radiation at atmospheric pressure, and the value 34.0 to B which with λ is a measure of the intensity of the F-number radiation in terms of the intensity of the penetrating primary radiation under specific conditions.

According to Eq. (6) we may choose K_2 which is a measure of the intensity of the C-number radiation, and K_3 which is a measure of the

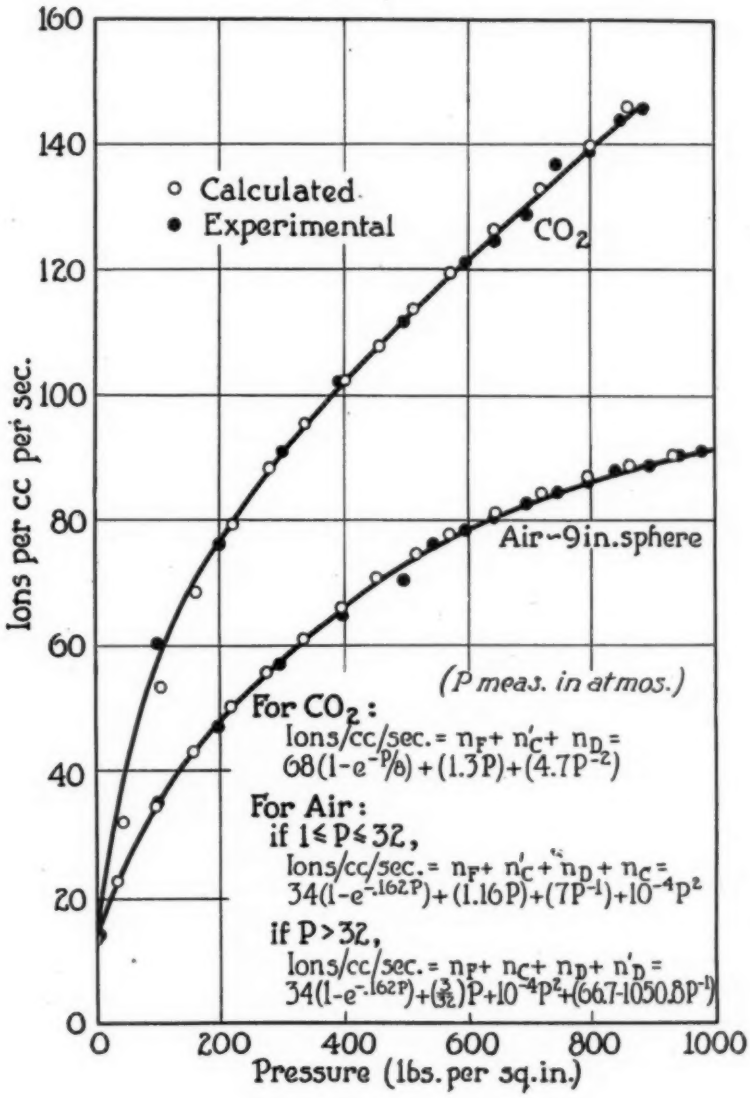
Ions per cc per sec.
Pressure (lbs. per sq.in.)
Calculated
Experimental
CO2
Air~9in.sphere
(P meas. in atmos.)
For CO2 :
Ions/cc/sec. = nF + n'C + nD =
68(1-e^-P/8) + (1.3P) + (4.7P^-2)
For Air:
if 1≤P≤32,
Ions/cc/sec. = nF + n'C + nD + nC =
34(1-e^-.162P) + (1.16P) + (7P^-1) + 10^-4 P^2
if P>32,
Ions/cc/sec. = nF + nC + nD + n'D =
34(1-e^-.162P) + (3/32)P + 10^-4 P^2 + (66.7-1050.8P^-1)

Fig. 4.

ionizing ability of the C-number radiation, in any way we like so long as we make $3\pi K_2 K_3 S = 0.552-$.

It is seen that Eqs. (10), (11) and (12) are not three equations defining three different K's, but that each pair defines K_9 if we assign values to

the G's. Luckily there is no conflict with the values we have had to assign to G_5, G_6 and G_7, and we are only required to let $K_9=63.44-$. Then K_7 and K_8 may be chosen as we like so long as $K_7K_8S=0.056$. It is very comforting to note that K_9 which represents the range of the D'-number rays at atmospheric pressure is very nearly 64 in terms of the radius of the sphere as unity. In accordance with our assumption, the D'-number radiation would therefore change to C'-number radiation at pressures below 32 atmospheres.

Turning to Eqs. (7), (8) and (9), we observe that we have here the same sort of relation as that existing among the group (10), (11) and (12). Here, however, we are not so fortunate. With the values we have found it advisable to assign to G_2, G_3 and G_4, there are no constant values for K_4, K_5 and K_6 which will satisfy the three equations simultaneously. We are led to conclude, therefore, that the D-number or tertiary radiations are themselves produced (and probably ionize) in a manner more complicated than we initially assumed. K_4, K_5 and K_6 may then be regarded not as constants, but as more complicated functions of the experimental conditions, which functions are so constituted that the G-functions of these may be regarded as constants. It should be noted that putting $G_2=.0001$ merely indicates that the term in P^2 has very little significance in the $P-n$ formulas.

By way of summary, we may recall that we have derived ionization formulas by assuming the ionization to be due to a single penetrating primary radiation and its consequent effects. These formulas give the pressure variation in air quite accurately, and at the same time they give the volume variation qualitatively. With the exception of those pertaining to the tertiary radiation, all the constants occurring in these formulas have been found capable of simple interpretation in terms of characteristics of the radiations at atmospheric pressure.

Oxygen was found to behave in much the same way as air. $P-n$ curves for carbon dioxide and nitrogen were found to differ from those for oxygen and air in that they became straight lines at their high pressure ends. In Fig. 4 is included an approximation for the case of carbon dioxide. It is seen that the observed pressure variation could be approximated closely throughout by the assumption of radiations of the F-, C'-, and D-numbers. The volume variation was not investigated in this case, nor was it determined experimentally. In Fig. 3 are included several curves which show how the ionization might, in general, be expected to depend upon the size of the spherical chamber if due to the various radiations considered, or to certain combinations of these.

The writer wishes to express his appreciation of the kind assistance of Dr. George Lynn and of Mr. F. C. Walz in checking certain calculations. Very sincere thanks are extended to Professor W. F. G. Swann whose encouragement and suggestions served in this as in many other instances, as the source of much inspiration.

HALE PHYSICAL LABORATORY,
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ATOMIC RADII. II[1]

By Maurice L. Huggins

Abstract

X-ray data show that *the two assumptions usually involved in previous calculations* of atomic radii from crystal structures—namely (1) that the distance between adjacent atomic centers in crystals equals the sum of the two atomic radii, and (2) that the radii of atoms of the same element in different crystals are equal—*in many cases cannot be correct.* Assuming that a valence electron pair can be assigned a definite position and *defining the atomic radius as the distance from the nucleus to a valence electron pair*, it is evident that (1) is only true when there is a valence pair on the straight line joining the centers of the adjacent atoms, and (2) should be true, or nearly so, only when the atoms of the given element are structurally similar and similarly surrounded in the two crystals. The probable arrangements of valence electrons in crystals, as deduced elsewhere by the author, are used in deciding as to the validity of the above assumptions in particular cases.

Comparable values of atomic radii have been calculated for a number of elements, in crystals in which atoms of these elements are each surrounded by *four* electronpairs at tetrahedron corners. Approximate radii of other elements similarly surrounded are obtained by interpolation and extrapolation. Radii are also calculated for certain elements in crystals in which each atom of these elements is surrounded by two, six, or eight electron pairs. The diameters of the hydrogen atom in six crystals are computed.

I. Introduction

IN 1920 W. L. Bragg[2] computed values for what he termed "atomic radii" and "atomic diameters" from crystal structure data. The chief assumptions underlying his calculations were: (1) that each atom of a given element is surrounded by a "sphere of influence" of the same size in different crystals; and (2) that the "spheres of influence" of adjacent atoms in crystals are tangent to one another.

Authors making similar calculations more recently,[3] realizing that these assumptions cannot both always be correct (Cf Table I), have assumed, in order to explain the x-ray data, atoms of irregular shapes or of different sizes (even though of the same element). They have, however, offered no criteria to use in determining when these assumptions are

[1] This is a revision of a paper written in 1922–23, while the author was a National Research Fellow at the University of California and Harvard University. Cf. Phys. Rev. **21**, 205 (1923).

[2] W. L. Bragg, Phil. Mag. **40**, 169 (1920); W. H. Bragg and W. L. Bragg, "X-Rays and Crystal Structure," G. Bell and Sons, London (1924).

[3] For references to work in this field, see Lunnon, Proc. Phys. Soc. London **38**, 93 (1926) or Davey, Chem. Rev. **2**, 349 (1925); Gen. Elec. Rev. **29**, 274 (1926).

near enough correct to warrant their use in calculating radii. Some such criteria are obviously necessary if atomic radii calculations are to be of much value.

TABLE I

Interatomic distance differences (A) in crystals of certain metallic halides

M	Li[4]	Na[4]	Cs[4]	Cu[5]	Cu[6]	Ag[7]
(M-Cl)−(M-F)	.56	.50				
(M-Br)−(M-Cl)	.18	.15	.15	.14	.17	.11
(M-I)−(M-Br)	.26	.26	.23	.12	.14	~.07

It has been shown by the writer[8] that if the valence electrons in the diamond and similar crystals are in constant orbital motion, in all probability they do not enclose whole atoms or pairs of atoms within their orbits but are in rotation about the atomic center-lines. With this picture (or with a picture of stationary or vibrating electrons[9]) we can evidently speak of an electron "position" in space, meaning the center of the orbit or the point about which the electron is oscillating.

It is generally accepted now that the valence shells of electronegative atoms in most chemical compounds contain eight electrons. A careful analysis[10] of known crystal structures has verified this conclusion and has also shown, what had already been shown to be very probable from chemical considerations,[11] that in many of these crystals, at least, the valence electrons are distributed in pairs at tetrahedron corners rather than singly at cube corners.

In view of the above, it is obvious that the "atomic radius," at least in so far as applied to crystal structure calculations, may be defined[12] as "the distance between the nucleus and the position occupied by a valence electron pair" (which we may designate as a point midway between the "positions" of the single electrons constituting that pair). With this definition, the interatomic distance equals the sum of the two atomic radii only when there is a valence pair on the straight line joining their centers. So if we know the distribution of these pairs in the crystal we can determine whether or not a given interatomic distance is suitable for the calculation of the atomic radii.

[4] Davey, Chem. Rev. **2**, 349 (1925); Gen. Elec. Rev. **29**, 274 (1926).
[5] Wyckoff and Posnjak, J. Am. Chem. Soc. **44**, 30 (1922).
[6] Davey, Phys. Rev. **19**, 248 (1922).
[7] Wilsey, Phil. Mag. **46**, 487 (1923).
[8] Huggins, Phys. Rev. **21**, 379 (1923); **27**, 286 (1926).
[9] Cf. Urey, Phys. Rev. **27**, 216 (1926).
[10] Huggins, Ref. 8.
[11] Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York (1923); Huggins, J. Phys. Chem. **26**, 601 (1922).
[12] Huggins, Phys. Rev. **19**, 346 (1922).

As regards the constancy of size of an atom of a given element in different crystals, it is evident from a consideration of the forces involved that the distance of a valence pair from the nucleus will depend on a number of factors[12]—the number of valence pairs around the kernel of the atom in question; the number and arrangement of electrons within the kernel; the number, kind or kinds, and arrangement of the surrounding atoms. In deciding whether the atoms of a given element are sufficiently similar in two crystals to make the assumption that the corresponding atomic radii in the two crystals are the same seem reasonable, use may again be made of the electron distributions shown elsewhere to be most probable, doubtful distributions being specifically mentioned as such. In general, these electron distributions depend on the following assumptions: (1) that the distribution of atomic centers as determined by x-rays is correct, (2) that the number of valence electrons per atom is as usually assumed by chemists and physicists, (3) that each electronegative atom (except in a very few crystals in which such an arrangement is impossible) has a valence shell consisting of four electron-pairs at tetrahedron corners, (4) that the valence tetrahedra are oriented, when possible, so as to place electron pairs on or near the centerlines between electropositive and electronegative atoms.

The author has shown[10] that in many cases the valence tetrahedra must be so oriented, while in all others (where the arrangement of atoms is known) the electron distribution around the kernels of the more positive atoms is at least as reasonable (usually more reasonable) with such an orientation as with any other orientation.

If we are to adhere to the limitations imposed by our definitions and the assumed structures, many crystal structure determinations are valueless for the calculation of accurate atomic dimensions. In fact, with no more data than are at present available, it is necessary, in order to get comparable values for more than a very few elements, to make approximations and assumptions which we know cannot be strictly true, but the attempt will be made, in this paper, to make these as few and as reasonable as possible, and to state definitely each assumption as it becomes involved in the calculations. Then, if later and better data show that some of these assumptions are in error, corrections can easily be made.

II. Radii of Atoms Having Four Electron Pairs in the Valence Shell

Our first calculations will deal only with crystals in which each atom of the element whose radius is being considered has a valence shell

consisting of four electron pairs at tetrahedron corners, these bonding it to four other kernels, the net charge on each of which is $(8-n)$ where n is the charge on the kernel of the central atom.

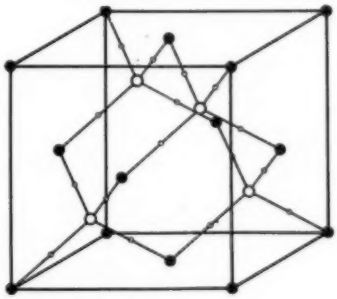

Fig. 1. The unit cube of the diamond—cubic ZnS type of structure. The large dots and circles represent the centers of Zn and S atoms respectively, or all C atoms. The small circles represent valence electron pairs. In crystals of the ZnS type these are closer to one kind of atom than to the other.

In the diamond, silicon, germanium, and gray tin, (Fig. 1) each atom is surrounded by four others at corners of a regular tetrahedron. Each kernel has a charge of +4 and the four valence electrons per atom are in pairs,[8] midway between adjacent atomic centers. The atomic radius is therefore in each case just half the interatomic distance. The values calculated are given in the last column of Table II.

TABLE II

Crystal	Interatomic distance	Atomic radius
C (diamond)	1.54A[13]	0.77A
Si	2.34[14]; 2.35[15, 16]; 2.36[17]	1.17; 1.18
Ge	2.43[18]; 2.44[19]	1.22
Sn (grey)	2.80[20]	1.40
SiC	1.90[21]	C = 0.77 (?); Si = 1.13 (?)

In crystals of silicon carbide, SiC, four silicon atoms are tetrahedrally distributed around each carbon, and four carbons are similarly disposed

[13] W. H. and W. L. Bragg, Proc. Roy. Soc. **A89,** 277 (1914).
[14] Gerlach, Phys. Zeits. **22,** 557 (1921); **23,** 114 (1922).
[15] Hull, Phys. Rev. **9,** 564 (1917); **10,** 661 (1917).
[16] Küstner and Remy, Phys. Zeits. **24,** 25 (1923).
[17] Debye and Scherrer, Phys. Zeits. **17,** 277 (1916).
[18] Kolkmeijer, Verslag. Akad. Wetenschappen **31,** 155 (1922); Proc. Roy. Acad. Sci., Amsterdam **25,** 125 (1922).
[19] Hull, Phys. Rev. **20,** 113 (1922).
[20] Bijl and Kolkmeijer, Chem. Weekblad. **15,** 1077, 1264 (1918); Proc. Roy. Acad. Sci., Amsterdam **21,** 501 (1919).
[21] Ott, Naturwissenschaften **13,** 76, 319, 644 (1925); Zeits. f. Krist. **61, 515 (1925); 62,** 201 (1925).

around each silicon. With valence electron pairs on the atomic centerlines, we should expect the Si-C distance (1.90A) to be equal to the sum of the carbon radius (0.77A) in the diamond and the silicon radius (1.17–1.18A) in elementary silicon, but we find this to be only approximately the case. Part of the difference may be due to experimental errors, but some of it must certainly be attributed to lack of constancy of the radii. As in many of the calculations to follow, we shall find it necessary to assume constant radii for a given element in different crystals when we have less reason to expect such constancy than in the substances just mentioned, we can obviously not expect our results to be in every case accurately correct. By means of various checks and calculations by different methods, however, we shall seek to make the errors as small as possible.

In proceeding to the calculation of atomic radii in other compounds, others have followed several different procedures; all of them, however, involve objectionable assumptions.

Pease[22] has assumed that all atoms having the same electronic arrangement (differing only in the charge on the nucleus) have practically the same radius. That this is not true is shown by a comparison of the interatomic distances in BeO (1.64–1.65A) and the diamond (1.54A), and in CuBr (2.49–2.52A) and Ge (2.43–2.44A), all of these substances having a similar arrangement around each atom in the crystal.

Davey[23] has assumed that Rb^+ and Br^- have the same radius, that being half of the interatomic distance in crystals of RbBr. Defining the atomic or ionic radius as the distance from nucleus to an electron pair in the outermost shell of each atom or ion, it is impossible for the electrons to be so disposed that the sum of the two radii, atomic or ionic, be equal to the interatomic distance in this crystal. Also, if the difference between the Cu and Ge radii is 0.05 to 0.09A greater or less than that between the Ge and Br radii, it would hardly seem likely that the Br^- and Rb^+ radii would be equal.

Wyckoff[24] prefers to start with the trihalides, such as $CsCl_2I$, in which three halogen atoms are on a straight line. Since the distance from the central halogen to each of the outer ones is obtained by intensity measurements, interpreted by means of assumptions which are known to be only qualitatively correct, it is not accurately known. A more important objection to transferring radii values calculated from these crystals to others, however, is that the number and arrangement of

[22] Pease, J. Am. Chem. Soc. **43**, 991 (1921).
[23] Davey, Phys. Rev. **18**, 102 (1921); **22**, 211 (1923); Ref. 3.
[24] Wyckoff, Proc. Nat. Acad. Sci. **9**, 33 (1923).

valence electrons around the central halogen is unknown and cannot be the same as in ordinary halogen compounds; so even if the iodine radius in $CsCl_2I$ were calculable, it may be, and probably is, quite different from that in other iodine compounds.

Another suggested procedure is to subtract the carbon radius, obtained from the diamond, from the carbon-oxygen distance in $CaCO_3$ or $MnCO_3$, to get the oxygen radius. Each carbon kernel in these compounds, however, is surrounded by *three oxygen* atoms, to which it is probably bonded by six electron pairs, none of which are on the atomic centerlines.[12] The carbon radius is therefore probably quite different in $CaCO_3$ from what it is in the diamond, and the sum of the carbon and oxygen radii cannot equal the interatomic distance.

One might also consider subtracting half the interatomic distance in a crystal of one of the metals, say Zn or Fe, from the distance between atoms in a crystal such as ZnS, or FeS_2, to obtain the sulfur radius; but the atomic radius, as here defined, is only calculable in the few metals in which the valence pairs are on the atomic centerlines, and in the compounds of these elements with non-metals for which the structures are known, the arrangements of electrons and atoms around each metal atom are quite different from what they are in crystals of the elements.

Quartz (SiO_2) will not serve as a suitable basis for atomic radii calculations, because the positions of the atoms are not known with sufficient accuracy, and because each oxygen is surrounded by *two tetravalent* atoms (instead of *four divalent* atoms).

There is but one other alternative with the data now available. In FeS_2[25] each sulfur kernel we may assume to be surrounded[26] by four electron pairs, these serving to bond it to three adjacent iron atoms and one adjacent sulfur atom. The parameter defining the S-S distance has been determined[27] probably as accurately as is possible by present methods; although just how accurate that is we have no way of knowing; there are assumptions involved in the determination (e.g. that the atoms can be treated as point scattering centers) which are known to be only approximations to the truth. The best we can do under the circumstances is to assume the computed interatomic distance (2.088A) to be correct, and halve it to get the distance from each sulfur nucleus to the valence pair between sulfur atoms. Here we meet with another difficulty. This sulfur radius is certainly greater—how much greater we do not know—

[25] W. L. Bragg, Proc. Roy. Soc. **A89**, 468 (1914).

[26] Huggins, Phys. Rev. **27**, 286 (1926); J. Am. Chem. Soc. **44**, 184 (1922).

[27] Ewald, Phys. Zeits. **15**, 399 (1914); Ewald and Friedrich, Ann. d. Physik **44**, 1183 (1914).

than the sulfur radius in a compound such as ZnS, where each sulfur is surrounded by four electropositive atoms. To emphasize the fact that it is necessary to make some assumption in regard to the magnitude of this difference, we shall arbitrarily assume it to be 0.024A in the calculations in this paper. This gives us the value 1.02A for the sulfur radius in ZnS and crystals similar to it. If this value is too low, then all the radii of electropositive atoms computed directly or indirectly from it in this paper are too high, and those of electronegative atoms are correspondingly too low, (provided the other assumptions involved are correct).

There are two simple types of crystal structure which binary compounds can possess in which each atom of one kind is surrounded by four of the other at tetrahedron corners. One of these is like the diamond structure, except that there are two kinds of atoms; the other has hexagonal symmetry and is usually known as the "zinc oxide type." X-ray analysis has shown that AlN, AlSb, ZnO, ZnS, ZnSe, CdS, HgS, BeO, CuCl, CuBr, CuI and AgI have one or the other (or both) of these structures.[28] The electrons in all of the above crystals may, on the basis of evidence previously presented,[8] be assumed to be in pairs on the centerlines between atoms, forming a tetrahedron of four pairs around each.

Comparisons of the interatomic distances in the sulfides, selenides and tellurides of zinc, cadmium and mercury (Table III) give us fairly concordant values (Table IV) for the radii of the component atoms. Too much faith must not be placed in the accuracy of these values, both because of the lack of satisfactory data and because the assumption that the radius of an atom is practically the same in different crystals may perhaps be incorrect. The checks obtained, on comparing the zinc and mercury compounds for instance, merely show that *if* the sulfur radius differs in ZnS and HgS, then the Se and Te radii in their compounds with Zn and Hg differ in the same way and about the same amount, and *if* the Zn radius changes in the series, sulfide, selenide, telluride, then the Hg radius changes similarly in the corresponding series of mercury compounds.

In the spinels, the general formula for which is $R''R'''_2O_4$ (R'' being an electropositive divalent element and R''' a positive trivalent element), each R'' atom is surrounded by four oxygen atoms at corners of

[28] Crystallographic data and interatomic distance comparisons (Huggins, Phys. Rev. **21**, 211 (1923)) make it seem very probable that ZnTe, CdSe, CdTe, HgSe and HgTe also have one or both of these two types of structure. The interatomic distances in these compounds, calculated from the densities on this assumption, have been included in Table III.

a regular tetrahedron, each R''' by six oxygen atoms at corners of an octahedron, and each oxygen atom by one R'' and three R''' atoms at tetrahedron corners. The valence electrons are in all probability in pairs on or very near the centerlines between adjacent atoms.[36] In the zinc spinels the arrangement of electrons and other atoms around each zinc kernel is precisely the same, and that of electrons and other atoms around each oxygen kernel is very nearly the same, as in ZnO. The Zn–O dis-

TABLE III

Crystal	Interatomic distance	Sum of radii (Table IV)
ZnO	1.96[29, 30]; 1.98A[31]	1.98A
ZnS	2.33[32]; 2.34[33]; 2.35[35]	2.35
ZnSe	2.45[34]	2.45
ZnTe	2.54[35]	2.56
$CdCr_2O_4$	(Cd-O) = 2.16; 2.18[36]	2.17
CdS	2.52[37]; 2.54[38]	2.54
CdSe	2.61[39]	2.64
CdTe	2.75[40]	2.75
HgS	2.53[41]; 2.54[42]	2.53
HgSe	2.63[43]	2.63
HgTe	2.73[44]	2.74
BeO	1.64[45]; 1.65[46]	1.64
$MgCr_2O_4$	(Mg-O) = 1.94; 1.96[36]	1.95
$MnCr_2O_4$	(Mn''-O) = 2.04; 2.06[36]	2.06
$FeFe_2O_4$	(Fe''-O) = 1.92; 1.94[36]	1.94
$CuFeS_2$	(Cu''-S) = 2.23–2.25[47]	2.23

[29] W. L. Bragg, Phil. Mag. **39**, 647 (1920).

[30] Aminoff, Zeits. f. Krist. **56**, 495 (1921); **57**, 204 (1922).

[31] Weber, ibid. **57**, 398 (1922).

[32] Aminoff, ibid. **58**, 203 (1923).

[33] Gerlach, Phys. Zeits. **23**, 114 (1922).

[34] Davey, Phys. Rev. **21**, 380 (1923).

[35] From density = 6.34 (Groth, "Chemische Krystallographie," Engelmann, Leipzig).

[36] Huggins, Phys. Rev. **21**, 509 (1923). The first of the two figures given for Cd-O, Mg-O, Mn''-O, and Fe''-O is in each case that calculated on the assumption that Zn-O in corresponding zinc compounds = 1.96A; in calculating the other it was assumed that Zn-O = 1.98A. The other assumptions involved are that the densities given by Groth (Ref. 35) are correct and that the R'''-O distance in different spinels is the same if the R''' atom is the same.

[37] Ulrich and Zachariasen, Zeits. f. Krist. **62**, 260 (1925).

[38] Davey, Phys. Rev. **19**, 248 (1922).

[39] From density = 5.80 (Groth, Ref. 35).

[40] From density = 6.20 (Margottet, Comptes Rendus **84**, 1293 (1877)).

[41] Kolkmeijer, Bijvoet and Karssen, Proc. Acad. Sci. Amsterdam **27**, 390, 847 (1924); Lehman, Zeits. f. Krist. **60**, 379 (1924); Olshausen, ibid. **61**, 463 (1925).

[42] Buckley and Vernon, Mineralog. Mag. **20**, 382 (1925).

[43] From density = 8.20 (Groth, Ref. 35).

[44] From density = 8.07 (Spencer, Mineralog. Mag. **13**, 268 (1904)).

[45] Aminoff, Zeits. f. Krist. **62**, 113 (1925).

[46] Zachariasen, Norsk geol. tidsskrift **8**, 189 (1925).

[47] From density = 4.196 and c/a = 0.9853 (Groth, Ref. 35), assuming (Fe''-S) = 2.29 – 2.31A.

tances should therefore be practically equal in the two cases. If we assume this, the oxygen atoms can be more accurately located in these crystals with reference to the other atoms than directly by x-ray means, and we can calculate the R'''–O distances. Then by transferring these to the Mg, Mn, Cd, and Fe spinels it is possible to obtain the R''–O distances and so the radii of these divalent atoms. The Cd–O distance obtained by this roundabout route (involving two possibly inaccurate density determinations) checks well with the sum of the radii calculated from CdS and ZnO.

TABLE IV

Li	Be	B	C	N	O	F	Ne	Na^+
1.16	0.99	0.86	0.77	0.70	0.65	0.61	0.58	0.56
Na	Mg	Al	Si	P	S	Cl	A	K^+
1.41	1.30	1.22	1.14	1.08	1.02	0.97	0.93	0.91
Cu	Zn	Ga	Ge	As	Se	Br	Kr	Rb^+
1.42	1.33	1.26	1.21	1.16	1.12	1.09	1.06	1.05
Ag	Cd	In	Sn	Sb	Te	I	Xe	Cs^+
1.62	1.52	1.43	1.36	1.29	1.23	1.19	1.16	1.14
Au	Hg	Tl	Pb	Bi				
1.60	1.51	1.42	1.36	1.3				

Mn'', 1.41; Fe'', 1.29; Cu'', 1.21.

Chalcopyrite, $CuFeS_2$, has been assigned a structure[48] similar to that of cubic zinc sulfide except for the replacement of half of the zinc atoms by copper and half by iron. From chemical considerations we should expect both copper and iron atoms to be divalent. Calculating the dimensions of the unit from the published density and axial ratio and assuming the iron-sulfur distance to be equal to the sum of the radii already computed (Table IV), we can calculate the copper-sulfur distance and from that obtain a value for the radius of the divalent copper atom.

Because of the marked disagreement between different observers in regard to the distances between atoms in the cuprous halides (Table V), the probable inaccuracy of the data on gray tin, and the disagreement between the values for the silicon radius calculated from silicon carbide and from elementary silicon, we cannot safely calculate directly the magnitudes of the atomic radii in these crystals and expect the results to be accurate and comparable with those already obtained. The values given for these radii in Table IV have been chosen so as to give smooth

[48] Burdick and Ellis, J. Am. Chem. Soc. **39**, 2518 (1917); Huggins, ibid. **44**, 1841 (1922).

curves when radii are plotted against atomic numbers (Fig. 2) and at the same time give Cu–X distances in fair agreement with the observed values. The silicon radius obtained from these curves agrees well with that from silicon carbide. The tin radius obtained by interpolation is not in good agreement with the experimental value. A discussion of possible reasons for this will be postponed until the experimental results have been checked.

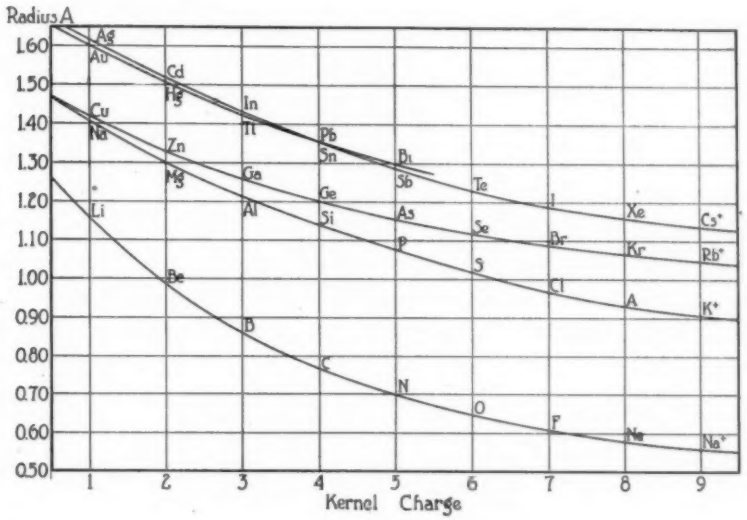

Fig. 2. Atomic radius—atomic number curves for atoms of kernel charge n bonded to four others of kernel charge $8-n$.

Subtracting our assumed iodine radius from what is probably the most accurately determined Ag–I distance in silver iodide, a figure is obtained for the silver radius which fits in well on the atomic radius—atomic number curve.

The radii of the elements in columns 3 and 5 of the periodic table can probably best be obtained from the curves of Fig. 2. Adding the appropriate radii, however, we get only a rough check with the experimental value for the interatomic distance in aluminum nitride and still poorer agreement in the case of aluminum antimonide (Table VI). The experimental results should be checked in order to determine whether there is actually as much variation of the radii as is indicated by these figures.

We can also obtain by extrapolation approximate values for the radii of the lithium, sodium, and fluorine atoms, in crystals comparable with the others discussed, as well as estimates of the distance from nucleus

TABLE V

Crystal	Interatomic distance	Sum of radii (Table IV)
CuCl	2.32[6]; 2.38A[5]	2.39A
CuBr	2.49[6]; 2.52[5]	2.51
CuI	2.61[49]; 2.63[6]; 2.64[5]	2.61
AgI	2.81[7, 50]; 2.83[6]	2.81
AuCl	2.56[51]	2.57

TABLE VI

Crystal	Interatomic distance	Sum of radii (Table IV)
AlN	1 89 A[52]	1.92 A
AlSb	2.65[53]	2.51

to outer shell in neon, argon, krypton and xenon. By further extrapolation we can very roughly estimate the magnitudes of the radii of certain of the electropositive *ions* (Table IV).[54]

Let us now turn to the study of crystals in which we can reasonably assume that the distance between atoms equals the sum of the atomic radii (i.e. in which the valence electron pairs are probably on or near the atomic centerlines) but in which we should expect radii differing from those already computed.

In Table VII are listed such interatomic distance data as are at present available for crystals of this kind. These data (as well as the data in Table VIII) all depend on the evaluation of one or more parameters. In general we should place less faith in their accuracy than in the accuracy of the interatomic distance determinations in crystals in which the atomic positions are fixed entirely by symmetry considerations and the dimensions of the unit cell.

[49] Aminoff, Geol. Fören. Förh. **44,** 197 (1922).

[50] Aminoff, Zeits. f. Krist. **57,** 180 (1922).

[51] From density = 7.4 [Rose, J. Chem. Soc. **67,** 905 (1895)]. There are available neither x-ray nor crystallographic data on the halides of monovalent gold. But if we assume this substance to possess one of the two structures possessed by ZnS, (or any other structure in which each ion is surrounded by four of the other kind at corners of a regular tetrahedron) the interatomic distance may be calculated from the density, and from this a tentative value for the Au radius. This comes out to be nearly the same as the Ag radius, just as the Hg radius was found to be practically equal to that of Cd. Such a result would seem to be quite improbable if the assumption in regard to the AuCl structure were incorrect. If a similar assumption were made regarding AgBr (which actually has the NaCl type of structure) for instance, the computed Ag radius would have been 1.44A, just 0.18A less than the value obtained from AgI.

[52] Ott, Zeits. f. Phys. **22,** 201 (1924).

[53] Owen and Preston, Proc. Phys. Soc. London **36,** 341 (1924).

[54] In this connection it may be noted that if we define the radius of an atom or ion as the distance from the nucleus to an electron pair in the outermost shell of that atom or ion, the *atomic* radius is the same as the *ionic* radius in the case of an electronegative ion, but not in the case of an electropositive ion.

TABLE VII

Crystal	Interatomic Distance	Sum of radii (Table IV)
As	2.51 A[55]	2.32A
Sb	2.87[56]; 2.92[57]	2.58
Bi	3.10[58]	2.6
Se	2.32[59]	2.24
Te	2.86[59]	2.46
As_4O_6	2.01[60]	1.81
Sb_4O_6	2.22[60]	1.94
SnI_4	2.63[61]	2.55
HgI_2	2.78[62]	2.70
SiO_2 (β-quartz)	1.62[63]	1.79
$C_6H_{12}N_4$	(C–N) = 1.44[64]	1.47
$BaSO_4$	(S–O) = 1.5[65]	1.67
$LiKSO_4$	(S–O) = 1.5–1.6[66]	1.67
$N_2H_6Cl_2$	(N–N) = 0.55–1.7[67]	1.40
C_2H_6	(C–C) = 1.5–1.6[68]	1.54
Ag_2MoO_4	(Mo–O) = 2.00[69]	——

It might be expected that the distance from nucleus to valence pair would be greater, other things being equal, the greater the kernel charge of the other atom holding to the valence pair in question; also that this distance would be greater the fewer other atoms surround the given atom, provided the number of electron pairs in the valence shell remains the same. So we should expect the radii of arsenic, antimony and bismuth, in crystals of the elements, in which each atom (having a kernel charge of +5) is bonded to three others of the same kind, to be greater than the radii obtained from the curves of Fig. 2. That this is the case is indicated by the experimental data (Table VII). Similarly in crystals of selenium and tellurium, in which each atom (having a kernel charge of +6) has a complete valence shell of four pairs, using two of them to bond it to other like atoms, the observed interatomic distances are considerably greater than twice the Se or Te radius in a crystal such as ZnSe or ZnTe. A similar situation exists in As_4O_6 and Sb_4O_6, in which all the atoms have

[55] Bradley, Phil. Mag. **47**, 657 (1924).
[56] James and Tunstall, ibid. **40**, 233 (1920).
[57] Ogg, ibid. **42**, 163 (1921).
[58] James, ibid. **42**, 193 (1921). Recalculated by McKeehan, J. Frank. Inst. **195**, 59 (1923).
[59] Bradley, Phil. Mag. **48**, 477 (1924).
[60] Bozorth, J. Am. Chem. Soc. **45**, 1621 (1923).
[61] Dickinson, ibid. **45**, 958 (1923).
[62] Huggins and Magill, from unpublished data.
[63] Wyckoff, Science **62**, 496 (1925); Am. J. Sci. **11**, 101 (1926).
[64] Dickinson and Raymond, J. Am. Chem. Soc. **45**, 22 (1923).
[65] James and Wood, Proc. Roy. Soc. **A109**, 598 (1925).
[66] Bradley, Phil. Mag. **49**, 1225 (1925).
[67] Wyckoff, Am. J. Sci. **5**, 15 (1923).
[68] Mark and Pohland, Zeits. f. Krist. **62**, 103 (1925).
[69] Wyckoff, J. Am. Chem. Soc. **44**, 1994 (1922).

tetrahedral valence shells, the arsenic or antimony atoms (kernel charge +5) being bonded each to three oxygen atoms (kernel charge +6) and the oxygen atoms each to two arsenic or antimony atoms. In the same category are SnI_4, in which each tin atom (kernel charge +4) is bonded to four iodines (kernel charge +7) and each iodine to but one tin, and HgI_2, in which each mercury atom (kernel charge +2) is bonded to four iodine atoms (kernel charge +7) and each iodine to two mercury atoms.

In β-quartz (SiO_2) each silicon is tetrahedrally surrounded by four oxygens and each oxygen is equidistant from two silicon atoms, two of the four oxygen valence electron pairs being presumably near the Si–O centerlines. We might here also expect the Si–O distance to be a little greater than the sum of the radii from Table IV, but according to Wyckoff's determination the reverse is the case. Possibly the valence pairs are far enough from the atomic centerlines to account for this.

A similar but smaller discrepancy exists in the case of hexamethylene tetramine, $C_6H_{12}N_4$, in which each carbon is bonded to one nitrogen and three hydrogen atoms and each nitrogen to three carbon atoms. The parameter determinations may perhaps be inaccurate enough to account for these results.

Accurate determinations of the distances between adjacent atoms in $BaSO_4$, $LiKSO_4$, $N_2H_6Cl_2$, and C_2H_6 have not been made.

The structure of silver molybdate, Ag_2MoO_4, is one in which each molybdenum atom is bonded to four oxygens and each oxygen to one molybdenum and three silver atoms. From the Mo–O distance, assuming the oxygen radius to be 0.65A, we get the value 1.35A for the radius of hexavalent molybdenum in this compound.

III. Radii of Atoms having Six Electron Pairs in the Valence Shell

Data for calculating radii of atoms having six electron pairs in their valence shells are fairly numerous but usually quite inaccurate. They are collected in Table VIII, together with the radii calculated therefrom on the assumption that the more negative atoms (to which the atoms in question are bonded) have the radii given in Table IV. This assumption is undoubtedly not strictly true, but the resulting errors are probably much less than the errors in the measurement of the distances between atoms, and some such assumption is necessary if we are to calculate these radii at all.

The figures in column 3 of Table VIII have been obtained directly by x-ray analysis, except in a few cases of which special mention is made in the footnotes. In many of the crystals listed the valence pairs are

TABLE VIII

	Crystal	Interatomic distance (observed)	Radii Assumed	Radii Calculated
Na–F	$NaHF_2$	2.36A[70]	F=0.61A	Na=1.75A
Na–O	$NaNO_3$	2.41[71]	O=0.65	Na=1.76
Mg–O	$Mg(OH)_2$	2.09[72]	O=0.65	Mg=1.44
Mg–O	$MgCO_3$	2.10[73]	O=0.65	Mg=1.45
Al–F	$(NH_4)_3AlF_6$	1.66[74]	F=0.61	Al=1.01
Al–O	$ZnAl_2O_4$	1.90; 1.92[75]	O=0.65	Al=1.25; 1.27
Al–O	Al_2O_3	1.84–1.99[76]	O=0.65	Al=1.19–1.34
Si–F	$(NH_4)_2SiF_6$	1.72[77]	F=0.61	Si=1.11
Ca–O	$CaCO_3$	2.37[78]	O=0.65	Ca=1.72
Cr'''–O	$ZnCr_2O_4$	1.99; 2.00[75]	O=0.65	Cr'''=1.34; 1.35
Mn''–O	$MnCO_3$	2.17[79]	O=0.65	Mn''=1.52
Mn''–O	$Mn(OH)_2$	2.19[80]	O=0.65	Mn''=1.54
Mn''–S	MnS_2	2.59[81]	S=1.02	Mn''=1.57
Fe''–O	$FeCO_3$	2.17[82]	O=0.65	Fe''=1.52
Fe''–S	FeS_2	2.25[83]	S=1.02	Fe''=1.23
Fe'''–F	$(NH_4)_3FeF_6$	1.9[74]	F=0.6	Fe'''=1.3
Fe'''–O	$ZnFe_2O_4$	2.02; 2.03[75]	O=0.65	Fe'''=1.37, 1.38
Ni''–N	$Ni(NH_3)_6Cl_2$	2.29–2.47[84]	N=0.70	Ni''=1.59–1.77
Ni''–N	$Ni(NH_3)_6I_2$	<2.64[84]	N=0.70	Ni''<1.94
Zn–O	$ZnCO_3$	2.12[73]	O=0.65	Zn=1.47
Zr–F	$(NH_4)_3ZrF_7$	1.77[85]	F=0.61	Zr=1.16
Mo^{IV}–S	MoS_2	2.41[86]	S=1.02	Mo^{IV}=1.39
Mo^{VI}–(O,F)	$(NH_4)_3MoO_3F_3$	1.9[74]	(O,F)=0.63	Mo^{VI}=1.27
Ag′–O	Ag_2MoO_4	2.31[87]	O=0.65	Ag′=1.66
Cd–O	$CdCO_3$	2.31[73]	O=0.65	Cd=1.66
Cd–I	CdI_2	3.00[88]	I=1.19	Cd=1.81
Sn^{IV}–Cl	K_2SnCl_6	2.44[89]	Cl=0.97	Sn=1.47
Sn^{IV}–Cl	$(NH_4)_2SnCl_6$	2.46[89]	Cl=0.97	Sn=1.49
Cs–Cl	$CsCl_2I$	3.65[90]	Cl=0.97	Cs=2.68
Pt^{IV}–Cl	$(NH_4)_2PtCl_6$	2.16–2.36[91]	Cl=0.97	Pt=1.19–1.39

[70] Rinne, Hentschel and Leonhardt, Zeits. f. Krist. **58**, 629 (1923).

[71] From $a=6.320$, $\alpha=48°6'$, $u=0.25$; Wyckoff, "The Structure of Crystals," p 349, Chemical Catalog Co., New York (1924).

[72] Aminoff, Geol. Fören. Förh. **41**, 405 (1919); Zeits. f. Krist. **56**, 506 (1921).

[73] In $MgCO_3$, $ZnCO_3$ and $CdCO_3$, the metal-oxygen distances have been computed from the densities and axial ratios given in Groth, Ref. 35, assuming the carbon-oxygen distance to be 1.26A.

[74] Pauling, J. Am. Chem. Soc. **46**, 2738 (1924).

[75] The two figures given are based on assumed values of the Zn-O distance of 1.98 and 1.96A, respectively. It is also assumed that the density given in Groth, Ref. 35, is correct.

[76] Pauling and Hendricks, J. Am. Chem. Soc. **47**, 781 (1925).

[77] Bozorth, ibid. **44**, 1066 (1922).

[78] From $a=6.360$A, $\alpha=46°6'$, $u=0.25$ (Wyckoff, Ref. 71, p. 357).

[79] From $a=5.836$A, $\alpha=47°45'$, $u=0.27$ (Wyckoff, Ref. 71, p. 358).

[80] Aminoff, Geol. Fören. Förh. **41**, 405 (1919).

[81] Calculated from density=3.463 (Gmelin-Kraut, "Handbuch der anorg. Chem.," (Winter, Heidelberg), **3** (2), 278) and $u=0.400$ (Ref. 27).

[82] From $a=5.822$A, $\alpha=47°45'$, $u=0.27$ (Wyckoff, Ref. 71, p. 358).

[83] From $a=5.38$A (Ref. 25) and $u=0.388$ (Ref. 27).

[84] Wyckoff, J. Am. Chem. Soc. **44**, 1239 (1922).

[85] Hassel and Mark, Zeits. f. Physik **27**, 89 (1924).

[86] Dickinson and Pauling, J. Am. Chem. Soc. **45**, 1466 (1923); Hassel, Zeits. f. Krist. **61**, 92 (1925).

probably not accurately on the centerlines between atoms, but the structures are such as to make it seem likely that the errors introduced on this account are small.

Comparing the metal-oxygen distance in crystals in which each metal atom is surrounded by (and bonded by single bonds to) four oxygens with its value in crystals in which there are six oxygens bonded to each metal atom, we find the latter to be the larger, as would be expected. (Compare the Mg, Mn'', Zn, and Cd radii in Tables IV and VIII.)

The Na, Mg and Al radii, in crystals in which each is bonded to six oxygens, form a gradually decreasing series, due no doubt to the changing kernel charge. (The 1.01A, 1.11A and 1.16A values for Al, Si and Zr, respectively, are probably considerably too low.)

Under corresponding circumstances we find the Ca radius considerably larger than that of Mg, and that of Cd larger than that of Zn. The Cs radius, in $CsICl_2$ is considerably larger than any of the others. These relationships are again as predicted from atomic theory.

Whether the two radii obtained for Fe'' are due to incorrect values of the interatomic distances, or to the difference between the arrangement around each Fe in FeS_2 and $FeCO_3$, or are the result of two types of kernel structure must be left to the future to decide.

The cadmium atom apparently has a greater radius when surrounded by six iodine atoms than when surrounded by six oxygens, probably chiefly because of the difference in the kernel charges of the iodine and oxygen.

Hexavalent molybdenum seems to have a smaller radius than tetravalent molybdenum, the larger kernel charge pulling the valence shell closer in. The data by themselves however are insufficient to make this certain. Similar reasoning in the case of the ferrous and ferric compounds would lead us to assume the larger value for the Fe'' radius to be more nearly correct than the other, unless there are two kinds of Fe'' atoms.

IV. Compounds having the Calcium Fluoride Type of Structure

The calcium fluoride structure is pictured in Fig. 3. If we assume the fluorine valence tetrahedra to be oriented so as to point toward the calcium atoms, then each of the latter is bonded to eight fluorines and

[87] Wyckoff, J. Am. Chem. Soc. **44**, 1994 (1922).
[88] Bozorth, ibid. **44**, 2232 (1922).
[89] Dickinson, ibid. **44**, 276 (1922).
[90] Wyckoff, ibid. **42**, 1100 (1920).
[91] Wyckoff and Posnjak, ibid. **43**, 2292 (1921).

each fluorine to four calciums. In Table IX have been listed the distances between adjacent atoms in this and other crystals of like structure, as well as the radii of the electropositive atoms, calculated on the assumption that the electronegative atoms have the radii given in Table IV.

The substances listed in Table X also have the calcium fluoride type of atomic arrangement, but in these each of the more negative atoms,

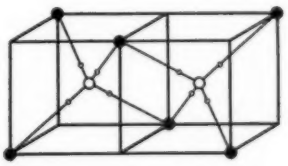

Fig. 3. Two adjacent eighth-unit cubes in the CaF_2 structure. The dots represent the centers of Ca atoms, the large circles F atoms, and the small circles valence electron-pairs.

TABLE IX

Crystal	Interatomic Distance	Radii Assumed	Radii Calculated
CaF_2	2.34[25]; 2.36[14]; 2.37[14]; 2.38A[6]	F=0.61A	Ca=1.73–1.77A
SrF_2	2.53[6]	F=0.61	Sr=1.92
$SrCl_2$	3.03[92]	Cl=0.97	Sr=2.06
BaF_2	2.69[6]	F=0.61	Ba=2.08
CeO_2	2.34[93]	O=0.65	Ce=1.69
ThO_2	2.41[93]	O=0.65	Th=1.76

TABLE X

Crystal	Interatomic Distance	Radii Assumed	Radii Calculated
Li_2O	2.00A[94]	O=0.65A	Li=1.35A
Li_2S	2.47[95]	S=1.02	Li=1.45
Na_2S	2.83[95]	S=1.02	Na=1.81
Cu_2S	2.45[96]	S=1.02	Cu=1.43
Cu_2Se	2.49[94]	Se=1.12	Cu=1.37
Ag_2S	2.63[97]	S=1.02	Ag=1.61
Ag_2Se	2.70[98]	Se=1.12	Ag=1.58
Ag_2Te	2.81[99]	Te=1.23	Ag=1.58
Mg_2Si	2.77[63]	Si=1.14	Mg=1.63
Mg_2Sn	2.92[100]; 2.94[101]	Sn=1.36	Mg=1.56; 1.58
Mg_2Pb	2.93[100]	Pb=1.36	Mg=1.57

[92] Mark and Tolksdorf, Zeits. f. Physik **33**, 681 (1925).

[93] Goldschmidt and Thomassen, Vidensk. Skrifter (1923), No. 2; Goldschmidt, Ulrich and Barth, ibid. (1925), No. 5.

[94] Bijvoet and Karssen, Rec. trav. chim. **43**, 680 (1924).

[95] Claasen, ibid. **44**, 790 (1925).

[96] From density=5.8 (Mellor, "Comprehensive Treatise on Theoretical and Inorganic Chemistry," Vol. III, Longmans, London (1923)).

[97] From density=7.27–7.32 (Groth, Ref. 35).

[98] From density=8.00 (Groth, Ref. 35).

[99] From density=8.32 (Groth, Ref. 35).

[100] Sacklovski, Ann. Physik **77**, 241 (1925).

[101] Pauling, J. Am. Chem. Soc. **45**, 2777 (1923).

if it has but four electron pairs in its valence shell, can be bonded to but four of the eight surrounding positive atoms (Fig. 4). The structure is

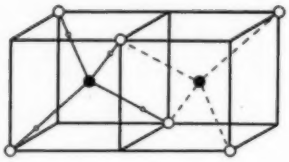

Fig. 4. Two adjacent eighth-unit cubes in the Li_2O structure. The dots represent the centers of Li atoms, the large circles O atoms, and the small circles electronpairs, in their most probable arrangement.

like that of cubic ZnS or CuCl with the insertion of a number of positive atoms equal to the number already present in such a way as to surround each by four of the more negative atoms. From Table X it may be seen that in the copper and silver compounds listed the distance between atoms is probably slightly less than the sum of the radii in Table IV, while in the similar lithium, sodium, and magnesium compounds the observed interatomic distances are considerably the greater.

V. Compounds having the Caesium Chloride Type of Structure

The caesium chloride structure (Fig. 5) may be thought of as being composed of two interlocking networks of the cubic ZnS type. Each atom, although surrounded at equal distances by eight others of opposite kind, is bonded by ordinary single bonds to but four of them. The interatomic distances and approximate radii of the component atoms are given in Table XI.

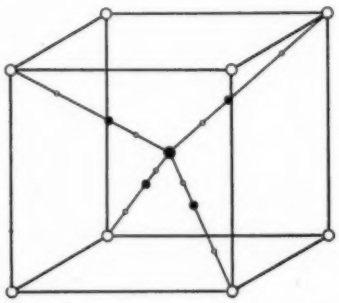

Fig. 5. The unit cube of the low temperature form of NH_4Cl. The large dot represents the center of an N atom; the smaller dots denote H atoms, the large circles Cl atoms, and the small circles electronpairs. This figure will also serve to represent the CsCl structure, the large dot and large circles denoting centers of Cs and Cl atoms, respectively.

Ammonium chloride and bromide crystallize similarly. From the interatomic distances and the halogen radii from Table IV we can calculate "radii" for the NH_4 group (*d*, Fig. 6) comparable with the atomic radii calculated for thallium and caesium.

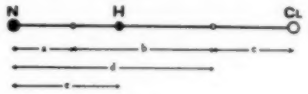

Fig. 6. The distribution of atomic centers and electronpairs along a N-Cl centerline in a crystal of NH_4Cl (low temperature form).

TABLE XI

Crystal	Interatomic Distance	Radii Assumed	Radii Calculated
CsCl	3.56[102]; 3.57A[103]	Cl=0.97A	Cs=2.59; 2.60A
CsBr	3.71[104]; 3.72[105]	Br=1.09	Cs=2.62; 2.63
CsI	3.94[106]; 3.95[106]; 3.97[107]	I=1.19	Cs=2.75; 2.76; 2.78
TlCl	3.32[108]; 3.33[109]	Cl=0.97	Tl=2.35; 2.36
TlBr	3.44[108]; 3.45[110]	Br=1.09	Tl=2.35; 2.36
NH_4Cl	3.34[111]; 3.35[102]; 3.36[112]	Cl=0.97	NH_4=2.37; 2.38; 2.39
NH_4Br	3.45[111]; 3.50[102]; 3.52[112]	Br=1.09	NH_4=2.36; 2.41; 2.43

VI. The Dimensions of the Hydrogen Atom in Crystals

Subtracting the nitrogen radius (*a*, Fig. 6) obtained from Table IV, from the NH_4 radii (*d*) in NH_4Cl and NH_4Br, we obtain what we might call the diameters (*b*) of hydrogen in these compounds. Since we do not know in either case the position of the hydrogen nucleus relative to the two nearest electron pairs we obviously cannot calculate the hydrogen "radii," nor can we calculate the radii (*e*) of the ammonium *ion*.

The probable structure of ice, according to W. H. Bragg, is like that of ZnO, with zinc atoms replaced by more oxygen and with a hydrogen midway between each pair of adjacent oxygens. The oxygen valence tetrahedra in such a structure we should expect to be oriented so as to place a corner (an electron pair) on each O–H centerline. The hydrogen

[102] Havighurst, Mack and Blake, ibid. **46**, 2368 (1924).
[103] Davey, Phys. Rev. **21**, 143 (1923).
[104] Davey, ibid. **19**, 538 (1922).
[105] Wyckoff, J. Wash. Acad. Sci. **11**, 429 (1921).
[106] Clark and Duane, Phys. Rev. **21**, 380 (1923).
[107] Davey, ibid. **18**, 102 (1921).
[108] Lunde, Zeits. f. Phys. Chem. **117**, 51 (1925).
[109] Davey and Wick, Phys. Rev. **17**, 403 (1921).
[110] Van Arkel, Physica **4**, 33 (1924).
[111] Bartlett and Langmuir, J. Am. Chem. Soc. **43**, 84 (1921).
[112] Vegard, Zeits. f. Physik **5**, 17 (1921).

diameter may then be obtained by subtraction, and from it the hydrogen radius in this substance. It is not surprising to find that in ice, which consists of but a single network of atoms (if the assumed structure is correct), the hydrogen diameter is somewhat less than in the ammonium halides, which are composed of two such networks interlocking with each other.

TABLE XII

Crystal	Interatomic distance	Assumed radii	Calculated hydrogen diameter
NH_4Cl	N–H–Cl = 3.34[111]; 3.35[102]; 3.36A[112]	N = 0.70; Cl = 0.97A	1.67; 1.68; 1.69A
$(H_3N–NH_3)Cl_2$	N–H–Cl = 3.14[67]	N = 0.70; Cl = 0.97	1.47
NH_4Br	N–H–Br = 3.45[111]; 3.50[102]; 3.52[112]	N = 0.70; Br = 1.09	1.66; 1.71; 1.73
H_2O	O–H–O = 2.76[113]	O = 0.65	1.46
KHF_2	F–H–F = 2.24 ± .16[114]	F = 0.61	1.02 ± .16
$NaHF_2$	F–H–F = 2.42[70]	F = 0.61	1.20

Another approximate value for the hydrogen diameter can be obtained from hydrazine dihydrochloride $(H_3N–NH_3)Cl_2$. The most probable hydrogen positions are near the N–Cl centerlines, each nitrogen being then surrounded tetrahedrally by four atoms. The N–Cl distance in Table XII has been calculated on the assumption that the N–N distance is 1.40A and that the parameter defining the chlorine positions has been correctly determined. If we postulate further that the N, H and Cl nuclei and the valence pairs between them are colinear (Fig. 6) and that the nitrogen and chlorine radii are as given in Table IV, we obtain a value (possibly quite inaccurate) for the hydrogen diameter which is practically the same as that calculated for ice.

In the structures which have been proposed for KHF_2 and $NaHF_2$ there is a hydrogen midway between each pair of fluorine atoms. Assuming again the correctness of the parameter determinations we obtain two more values of the diameter of hydrogen.

Some of the variability in the values calculated for this distance from different crystals results no doubt from inaccurate data and incorrect assumptions, but part of it must probably be attributed to a real difference in size in different types of compounds. Surely we should expect such variation.

[113] W. H. Bragg, Proc. Phys. Soc. **34**, 98 (1922).
[114] Bozorth, J. Am. Chem. Soc. **45**, 2128 (1923).

VII. Compounds having the Cuprous Oxide Arrangement

Cu_2O and Ag_2O crystallize with a structure (Fig. 7) in which each oxygen atom is surrounded tetrahedrally by four metal atoms and each metal atom is midway between two oxygen atoms. If the oxygen valence

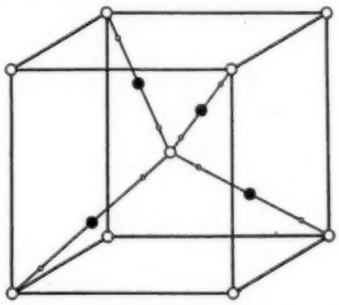

Fig. 7. The unit cube of Cu_2O. The large dots and circles represent the centers of Cu and O atoms respectively. One of the possible distributions of valence electron pairs (small circles) is shown.

tetrahedra have their corners oriented toward the neighboring Cu or Ag atoms, we can calculate the radii of Cu and Ag atoms containing but two electron pairs in the valence shell. As would be expected, these (Table XIII) are much less than the corresponding radii in Table IV.

VIII. Elements having the Body-Centered Cubic Structure

The probable structure of chromium, molybdenum and tungsten (Fig. 8) is one consisting of two interpenetrating simple cubic networks

Table XIII

Crystal	Interatomic distance	Radii Assumed	Radii Calculated
Cu_2O	1.84[6, 115]; 1.86 A[116]	O=0.65A	Cu=1.19; 1.21A
Ag_2O	2.03[6]; 2.04[115]; 2.06[117]	O=0.65	Ag=1.38; 1.39; 1.41

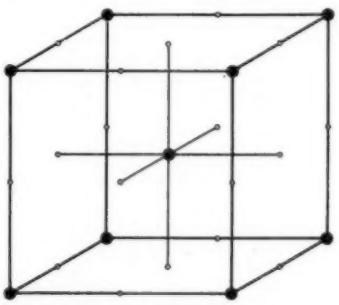

Fig. 8. Unit cube of the Cr, Mo or W crystal.

[115] Niggli, Zeits. f. Krist. **57**, 253 (1922).
[116] W. H. Bragg and W. L. Bragg, Ref. 2; Greenwood, Phil. Mag. **48**, 654 (1924).
[117] Wyckoff, Am. J. Sci. **3**, 184 (1922).

of atoms, each atom being bonded by single bonds not to the eight nearest atoms but to the six others at a slightly greater distance. The radii obtained from such crystals (Table XIV) are comparable with each other but cannot reasonably be expected to agree with corresponding radii in other types of structure.

TABLE XIV

Crystal	Interatomic distance	Radius
Cr	2.88A[118]	1.44A
Mo	3.08[119]; 3.14[120]	1.54; 1.57
W	3.15[121]; 3.18[122]	1.58; 1.59

IX. LEAD MONOXIDE

In lead monoxide, PbO, each oxygen is tetrahedrally surrounded by four lead atoms and each lead atom is at the apex of a pyramid having four oxygen atoms at its base. The Pb–O distance has been given[123] as 2.33A. If the valence pairs are on the atomic centerlines the Pb'' radius is then about 1.68A, considerably greater (as might be expected) than that extrapolated for Pb^{IV} from Fig. 2.

TABLE XV

Crystal	Interatomic distance
CO_2	(C=O) = 1.05[124]; 1.25[125]; 1.59[126]
$CaCO_3$	(C=O) = 1.25[127]
$MnCO_3$	(C=O) = 1.27[128]
$NaNO_3$	(N=O) = 1.29[129]
N_2O	(N=O) or (N=N) = 1.15[130]
NaN_3	(N=N) = 1.17[131]
KN_3	(N=N) = 1.16[131]
KCN	(C≡N) = 1.15[132]

[118] Patterson, Phys. Rev. **26,** 56 (1925); Davey and Wilson, ibid. **27,** 105 (1926).

[119] Stoll, Arch. Sci. Phys. Nat. **3,** 546 (1921).

[120] Davey, Phys. Rev. **25,** 753 (1925); Fischvoigt and Koref, Zeits. f.Techn. Phys. **6,** 296 (1925).

[121] Davey, Ref. 120. Davey and Wilson, Ref. 118.

[122] Debye, Phys. Zeits. **18,** 483 (1917); Fischvoigt and Koref. Ref. 120.

[123] Dickinson and Friauf, J. Am. Chem. Soc. **46,** 2457 (1924).

[124] DeSmedt and Keesom, Proc. Acad. Sci. Amsterdam **27,** 839 (1924); Zeits. f. Krist. **62,** 312 (1925).

[125] McLennan and Wilhelm, Trans. Roy. Soc. Can., Sec. III (3), **19,** 51 (1925).

[126] Mark and Pohland, Zeits. f. Krist. **61,** 293 (1925).

[127] From $a = 6.360$A, $\alpha = 46°6'$, $u = 0.25$ (Wyckoff, Ref. 71, p. 357).

[128] From $a = 5.836$A, $\alpha = 47°45'$, $u = 0.27$ (Wyckoff, Ref. 71, p. 358).

[129] From $a = 6.320$A, $\alpha = 48°6'$, $u = 0.25$ (Wyckoff, Ref. 71, p. 349).

[130] DeSmedt and Keesom, Proc. Acad. Sci. Amsterdam **27,** 839 (1924).

[131] Hendricks and Pauling, J. Am. Chem. Soc. **47,** 2904 (1925).

[132] Bozorth, ibid. **44,** 317 (1922).

IX. Double and Triple Bonds

Table XV contains the various values calculated from x-ray data for the distances between atoms which are probably connected by double or triple bonds. These are all very approximate except perhaps the C=O and N=O distances in $CaCO_3$, $MnCO_3$ and $NaNO_3$. In these compounds each C or N is probably joined by double bonds to three surrounding oxygen atoms.[12] In CO_2 and N_2O the central atom is probably connected by double bonds to the other two atoms. In KCN the CN groups (or "ions") are related to the potassium "ions" in the crystal only as the "ions" of chlorine are related to those of sodium in crystals of NaCl. So also in KN_3 and NaN_3 the structural units are the K^+, Na^+ and N_3^- ions. The two end nitrogens of the N_3^- ion seem to be equivalent; if each of the three has a valence shell containing eight electrons the structure must then be $\left(:\ddot{N}-\ddot{N}-\ddot{N}:\right)^-$.[133]

Theory would lead one to expect smaller distances, in general, between two atoms joined by a double or triple bond than between the same atoms joined by a single bond. This seems to be the case.

In conclusion the author wishes to point out again the tentative nature of the results given in this paper and their limited applicability. It is believed, however, that when properly used they will prove of greater value than atomic and ionic "radii" calculated without regard to the electronic structures of the crystals concerned. Helpful suggestions from Professor Wm. C. Bray of the University of California are gratefully acknowledged.

Stanford University,
March 19, 1926.

[133] Hendricks and Pauling, Ref. 131, prefer the structure $\left(:\ddot{N}:\ddot{N}:\ddot{N}:\right)^-$ for the trinitride ion.

INTENSITIES IN THE STARK EFFECT OF HELIUM

By Jane M. Dewey[1]

Abstract

Theory of the intensity of combination lines in the Stark effect.—The quantum theory of dispersion may be applied to the Stark effect in a weak field by considering the atoms exposed to external radiation of zero frequency. This makes it possible to calculate the intensity of new lines appearing in the field (combination lines) from the intensity of lines appearing in the undisturbed spectrum. The theory is applied here to the helium spectrum.

Measurements of the intensity of combination lines of He in the Stark effect.—Measurements of the intensity of the helium lines $2P-nM$, $2P-nm$, $2S-4M$, where $n=4, 5, 6, 7$; $M=P, D, F$, etc., are given. The Lo Surdo method of obtaining emission in an electric field was used, with the cathode set with its surface parallel to the slit of the spectrograph. A photographic method of measuring the intensities, using a Moll photometer to measure the photographic density was used. The intensity of the combination lines increases as the square or higher powers of the electric field, as the theory demands. The ratio of the intensity of the combination lines to the nearest lines in the spectrum emitted by the undisturbed atom is in approximate agreement with that calculated from the theory.

Introduction

ONE of the first phenomena to receive an explanation on the basis of the quantum theory of atomic structure was the Stark effect. Epstein[2] and Schwarzschild[3] showed that the observed splitting up of the Balmer lines in an electric field[4] received a simple explanation on the basis of the Bohr theory of the atom. Later Kramers[5] was able to estimate the intensities of these lines from the correspondence principle. According to Stark's[6] experiments the effect of an electric field on the spectrum of other elements is essentially different from its effect on the hydrogen spectrum. The lines of these spectra show, in general, no splitting up proportional to the first power of the electric field, but the spectra show new lines the frequencies of which are sums or differences of the frequencies of lines in the original spectrum. Bohr[7] pointed out that these facts received a simple explanation on the quantum theory,

[1] International Fellow of Barnard College, Columbia University.

[2] Epstein, Ann. d. Physik **50**, 189 (1916).

[3] Schwarzschild, Ber. Akad. Wiss., Berlin, 548 (1916).

[4] Stark, Ber. Akad. Wiss., Berlin **47**, 932 (1913).

[5] Kramers, Det Kgl. Danske Videnskabernes Selskabs Skrifter **8**, III, 278 (1919).

[6] Stark, Monograph "Elektrische Spektralanalyse chemischer Atomen," Leipzig, 1914.

[7] Bohr, Det Kgl. Danske Videnskabernes Selskabs Skrifter **8**, IV, 1.

and that the intensity of the new lines should be, in the first approximation, proportional to the square of the field intensity. Pauli[8] has shown that for weak fields the appearance and intensity of these lines may be treated by the quantum theory of dispersion proposed by Kramers.[9] He discussed the observations of Hansen, Takamine and Werner[10] on the spectrum of mercury in an electric field on the basis of this theory and showed that they were in substantial agreement with it.

The Stark effect in helium has been subjected to careful examination by various investigators.[11] Recently Takamine and Werner[12] have given the results of measurements of the intensities of combination lines in the helium spectrum made in such a way as to obtain a direct check on the theory. Their measurements were carried out by photographic methods developed in the laboratory of the University of Utrecht. The research reported here is a continuation of their work. It is planned to give, in this and succeeding articles, measurements of the intensities of all helium lines which are of interest to the theory.

Theory of the Intensities of Combination Lines

The application of the theory of dispersion to the Stark effect allows the calculation of the intensities of combination lines from the amplitudes appearing in the quantum theory description of the undisturbed atom, or conversely the calculation of these amplitudes from measurements of the intensity of combination lines.

We shall describe the spectrum with three quantum numbers, n, k, j. The lines appearing in the absence of a field are described by $n'-n''$ arbitrary, $k'-k''=\pm 1$, $j'-j''=0$ or ± 1, where n' is the value of n in the initial and n'' the value of n in the final state and k', j' are similarly defined. This is to be expected from the correspondence principle if we represent the motion in the atom by a precessing Kepler ellipse and carry this description of the motion directly into the quantum mechanics. When the atom is exposed to an external field of force the correspondence principle predicts that new harmonic components will appear in the motion because of the disturbance caused by the field. These components correspond to transitions for which the rules of selection for k and

[8] Pauli, Det Kgl. Danske Videnskabernes Selskabs Medd. **7**, 3 (1925).

[9] See especially Kramers and Heisenberg, Zeits. f. Physik **31**, 681 (1925). Cf. also Born, Heisenberg and Jordan, Ibid. **35**, 567 (1926) where the dispersion formula is derived from the quantum mechanics.

[10] Takamine and Werner, Det Kgl. Danske Vidensk. Selsk. Medd. **5**, 3 (1923).

[11] Stark, reference 5. Koch, Ann. d. Physik **48**, 98 (1919); Tschulanowsky, Zeits. f. Physik **16**, 300 (1923); Foster, Phys. Rev. **23**, 667 (1924).

[12] Takamine and Werner, Naturwiss. **14**, 348 (1925).

j do not hold. The intensity of lines whose frequencies are equal to the sum or difference of the frequencies of two lines in the original spectrum i.e., those for which k changes by 0 or 2, increases as the square of the field. The intensity of lines corresponding to a change of k of more than two increases as some higher power of the field. A quantitative determination of the probabilities of transition may be obtained by comparison with the quantum theory of dispersion, since, according to the quantum mechanics, the action of an oscillating field on an atom must approach the action of a constant field as the frequency of the oscillating field approaches zero.

To carry through the application of the dispersion theory it is convenient to consider a non-degenerate system. We may remove the degeneracy with respect to orientation in space by imagining the atom exposed to a very weak magnetic field, of axis parallel to the electric field we are going to apply. The magnetic field is to be so weak that it does not change the motion in the atom nor affect the rules of selection. For a complete description of the motion we must now introduce a magnetic quantum number m, which describes the orientation with respect to the field and which may change by 0 or ± 1. In transitions involving no change of m the emitted radiation is polarised parallel to the field. The radiation emitted in transitions in which m changes by ± 1 is circularly polarised in a plane perpendicular to the field. The formula giving the polarisation and intensity of combination lines whose frequency is the sum or difference of two lines in the original spectrum is

$$\boldsymbol{A}(p,r)\, e^{2\pi i \nu(p,r) t} = \frac{1}{2h} \Sigma_q \left[\frac{\boldsymbol{A}(p,q)(\boldsymbol{E}\boldsymbol{A}(q,r))}{\nu(q,r)} - \frac{\boldsymbol{A}(q,r)(\boldsymbol{E}\boldsymbol{A}(q,p))}{\nu(p,q)} \right] e^{2\pi i [\nu(q,r)+\nu(p,q)] t} \tag{1}$$

where $\boldsymbol{A}(p, r)$ is a vector, in general complex, which represents the so-called characteristic amplitude of the transition state p to state r. It is so defined that the real part of the expression on the left side of the equation is the electric moment we must ascribe to the atom to account for the radiation of frequency $\nu(p, r)$ emitted. h is Planck's constant, the amplitudes $\boldsymbol{A}(p, q)$ $\boldsymbol{A}(q, r)$ are defined similarly to $\boldsymbol{A}(p, r)$ but refer to the amplitude of the corresponding transitions in the undisturbed atom. $\boldsymbol{E}$ is the field strength, considered as a vector quantity. The summation is to be extended over all states r for which the transitions, p, q and q, r are permitted by our rules of selection. The formula follows directly from the general formulas of the quantum theory of

dispersion if the frequency of the external radiation is set equal to zero.[13] The energy emitted in the form of radiation of the frequency $\nu(p, q)$ per atom per second is given by the formula

$$I=\frac{[2\pi\nu(p,q)]^4}{c^3}\,\boldsymbol{A}(p,q)\boldsymbol{A}(q,p) \tag{2}$$

$\boldsymbol{A}(q,p)=\bar{\boldsymbol{A}}\,(p, q)$ where $\bar{\boldsymbol{A}}$ represents the vector conjugate to $\boldsymbol{A}$. Because of the appearance of a frequency ν in the denominator of both terms of formula (1) certain terms in the infinite sum represented by the general formula will be of a greater order of magnitude than all of the others and need alone be considered.

In considering the new lines whose intensities vary as powers of $\boldsymbol{E}$ higher than the square we shall confine ourselves to those lines whose frequencies are combinations of three lines in the spectrum emitted in the absence of the field. In this case the polarisation and amplitude of the line are given by

$$\begin{aligned}\boldsymbol{A}(p,s)e^{2\pi i\nu(p,s)}=\frac{1}{4h^2}\sum_r\sum_q\Bigg[&\frac{\boldsymbol{A}(p,q)((\boldsymbol{EA}(q,r))((\boldsymbol{EA}(r,t))}{\nu(q,t)\nu(r,t)}\\ +&\frac{\boldsymbol{A}(q,r)(\boldsymbol{EA}(r,s))(\boldsymbol{EA}(p,q))}{\nu(p,q)\nu(r,s)}+\frac{\boldsymbol{A}(r,s)(\boldsymbol{EA}(p,q))(\boldsymbol{EA}(q,r))}{\nu(q,r)\nu(q,t)}\Bigg]\\ &\cdot e^{2\pi i[\nu(p,q)+\nu(q,r)+\nu(r,s)]t}\end{aligned} \tag{3}$$

This formula is obtained directly as the second approximation of the theory of perturbations of the quantum mechanics, as formula (1) may be obtained as the first approximation of this theory.[14] Because of the appearance of two frequencies in the denominator, in making the summation, only such states need be taken into consideration as give at least one term in which both ν values are small.

Application of the Theory

In order to illustrate the application of formula (1) let us consider the calculation of the intensity of the parallel and perpendicular components of the line $2P-4P$ in parhelium. In Fig. 1 the terms of the helium spectrum are represented by points in the usual way, the values of the terms being proportional to the distances of the points from the vertical line on the right. The transition $4P$, $2P$ is shown by a dotted line, while the pairs of transitions by combination of which the transition

[13] Kramers and Heisenberg, ref. 9, formula (32). Cf. also Pauli, ref. 8, formula (5).
[14] See Born, Jordan and Heisenberg, ref. 9, p. 566.

$4P$, $2P$ can be obtained are shown by the solid lines. It is seen that the only terms to be used in formula (1) are those whose denominators are $\nu(4P, 4D)$ and $\nu(4P, 4S)$. But $\nu(4S, 4P)$ is twelve times $\nu(4P, 4D)$ and the numerator of the term of which it is the denominator is smaller than the numerator of the other term, so we may discard the term of which $\nu(4S, 4P)$ is the denominator. In order to apply formula (1) we must remember that in the magnetic field the states $2P$ and $4P$ consist each of three states ($m=-1, 0, +1$) and the state $4D$ consists of 5 states

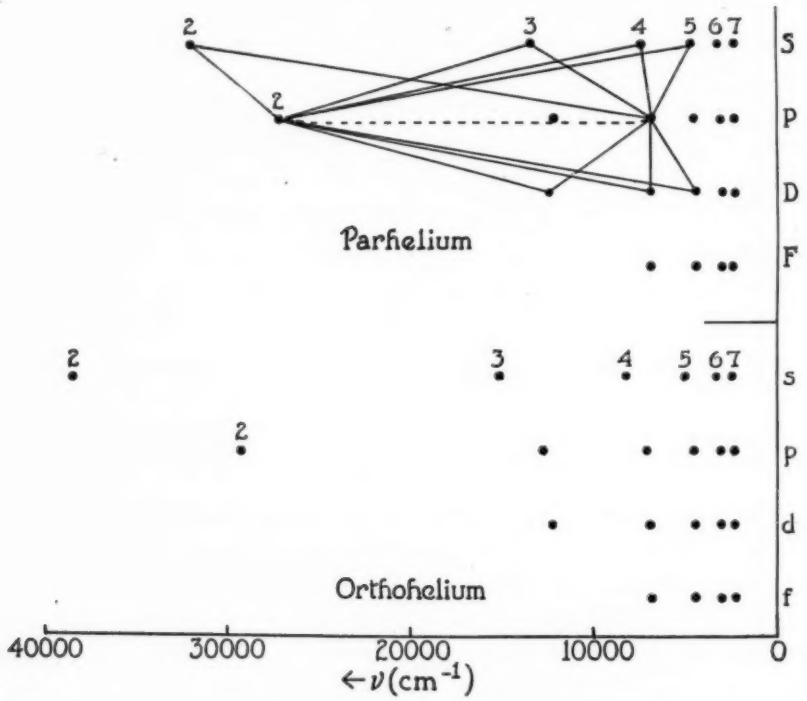

Fig. 1. The terms of the helium spectrum with the transitions giving $2P-4P$.

($m=-2, -1, 0, +1, +2$). The only q, r transitions which contribute to the sum on the right side of formula (1) are those for which m remains unchanged, since for these transitions $\boldsymbol{A}$ and $\boldsymbol{E}$ are parallel, while for transitions in which m changes by one unit $\boldsymbol{A}$ and $\boldsymbol{E}$ are perpendicular, and their scalar product, appearing in the formula, is zero. Writing the m values as subscripts to the terms we obtain

$$A(4P_{m'}, 2P_{m''}) = \frac{E}{2h} \frac{A(4D_{m'}, 4P_{m'})A(4D_{m'}, 2P_{m''})}{\nu(4D, 4P)} \tag{4}$$

The ratios of the intensities of the transitions corresponding to different m' and m'' values for a given line are known from the formula of Kronig, Goudsmit and Honl.[15] Since it may be assumed that there are the same number of atoms in each $4P_m$ state and in each $4D_m$ state, we also know the ratio of the amplitudes to each other, and may express them all in

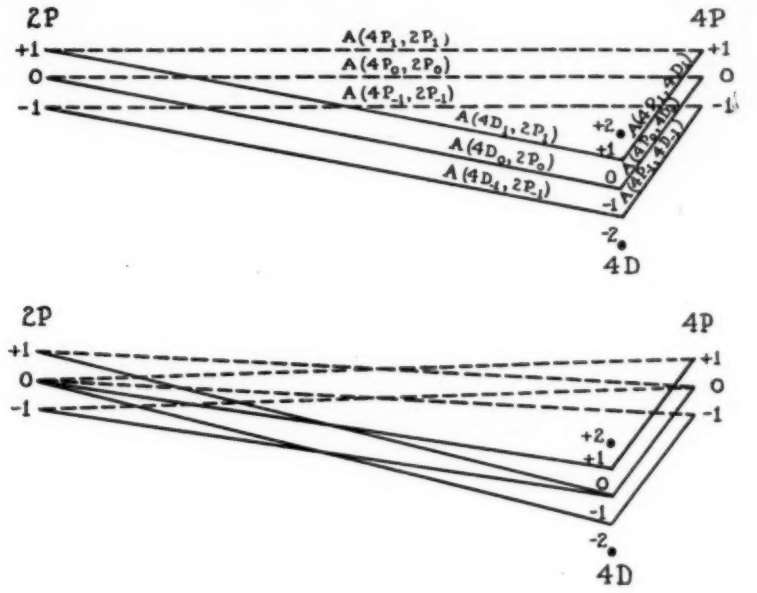

Fig. 2. Transitions used in calculating the intensity of the line $2P-4P$.

terms of $A(4D_0, 2P_0)$ and $A(4D_0, 4P_0)$. If we introduce the assumption that the number of atoms in a $4P_m$ state and a $4D_m$ state are the same, it is seen that the ratio $I^\tau(4P, 2P)/I^\tau(4D, 2P)$[16] which has been the subject of the measurements depends only on E, $\nu(4D, 4P)$ and $A(4D_0, 4P_0)$. Since we know the field this latter amplitude can be calculated from the intensity measurements and compared with the theoretical value. The numerical calculation follows.

$$A(nP\pm1, 4D\pm1)^2 = \tfrac{3}{4}A(nP_0, 4D_0)^2 \quad (5)$$

$$A(nP_0, 4D\pm1)^2 = \tfrac{3}{8}A(nP_0, 4D_0)^2 \quad (6)$$

$$A(nP\pm1, 4D_0)^2 = \tfrac{1}{8}A(nP_0, 4D_0)^2 \quad (7)$$

$$I^\tau(4P, 2P) = K\nu(4P, 2P)^4 \frac{E^2}{4h^2} \frac{A(4P_0, 4D_0)^2 A(4D_0, 2P_0)^2}{\nu(4P, 4D)^2} [2(\tfrac{3}{4})^2 + 1] \quad (8)$$

[15] See, for instance, Kronig, Zeits. f. Physik **31**, 885 (1925).

[16] I^τ represents the intensity of the parallel component of a line and I^σ of the perpendicular component.

$$I^{\tau}(4D,2P)=K\nu(4D,2P)^4A(4P_0,2P_0)(2\cdot\tfrac{3}{4}+1)=I^{\sigma}(4D,2P) \tag{9}$$

where K is a constant containing the proportionality factor of formula (2) and the number of atoms in the initial states ($4P_m$ and $4D_m$). Since $\nu(4P,\ 2P)=\nu(4D,\ 2P)$ to a good approximation

$$\frac{I^{\tau}(4P,2P)}{I^{\tau}(4D,2P)}=\frac{E^2}{4h^2}\,\frac{A(4P_0,4D_0)^2}{\nu(4P,4D)^2}\,\frac{17}{20} \tag{10}$$

Also

$$I^{\sigma}(4P,2P)=K\nu(4P,2P)^4\frac{E^2}{4h^2}\,\frac{A(4P_0,4D_0)^2A(4D_0,2P_0)^2}{\nu(4P,4D)^2}2(\tfrac{3}{4}\cdot\tfrac{3}{8}+\tfrac{1}{8}) \tag{11}$$

So that

$$\frac{I^{\tau}(4P,2P)}{I^{\sigma}(4P,2P)}=2.6 \tag{12}$$

Similar calculations for the intensity of the line $2S-4D$, give

$$\frac{I^{\tau}(4D,2S)}{I^{\tau}(4D,2P)}=\frac{E^2}{4h^2}\,\frac{A(4P_0,4D_0)^2}{\nu(4P,4D)^2} \tag{13}$$

and

$$\frac{I^{\tau}(4D,2S)}{I^{\sigma}(4D,2S)}=1.3 \tag{14}$$

From calculations of the intensity of the line $2P-4F$ we obtain

$$\frac{I^{\tau}(4F,2P)}{I^{\tau}(4D,2P)}=\frac{E^2}{4h^2}\,\frac{A(4F_0,4D_0)^2}{\nu(4D,4F)}\,\frac{14}{15} \tag{15}$$

$$\frac{I^{\tau}(4F,2P)}{I^{\sigma}(4F,2P)}=1.3 \tag{16}$$

If we apply the second approximation formula to the intensity of $2S-4F$ we obtain

$$\frac{I^{\tau}(4F,2S)}{I^{\tau}(4P,2S)}=\frac{E^4}{16h^4}\,\frac{A(4P_0,4D_0)^2A(4D_0,4F_0)^2}{\nu(4P,4D)^2\nu(4D,4F)^2} \tag{17}$$

To deal with the orthohelium lines we shall assume that they are unresolved triplets. In Fig. 3 the resolution of the p and d terms into their j and m values is given. The ratios of the various $A(np_{m'j'},\ 4p_{m''j''})$ to each other is found as for parhelium from the formulas of Kronig. The calculations are more complicated because of the large number of

transitions possible. Instead of going through the entire calculation for $2p-4p$ we shall give in detail only the calculation for $2p_1-4p_1$ $m'=0\rightarrow m''=0$. The transitions used in this calculation are drawn in Fig. 3. The calculations for the other transitions are made in the same way and the squares of the amplitudes summed as for parhelium. We

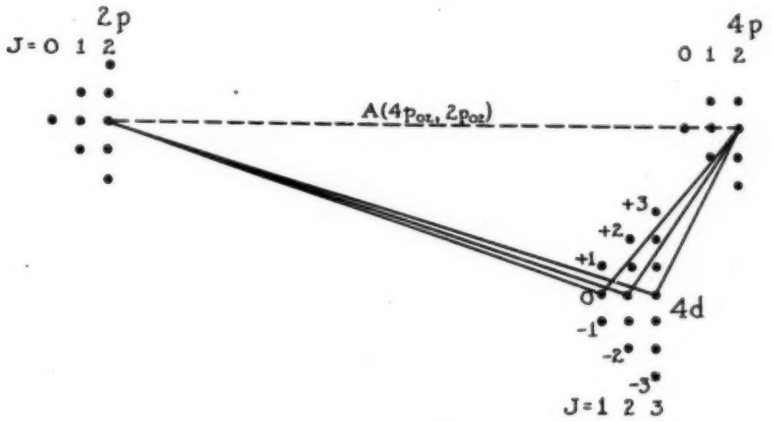

Fig. 3. Transitions used in calculating the intensity of $2p_1-4p_1$, $m=0\rightarrow m=0$.

shall neglect the terms containing $\nu(4s, 4p)$, $\nu(5s, 4p)$ or $\nu(5d, 4p)$ as this introduces only a slightly larger error than the neglect of corresponding terms in the calculation for parhelium. If we write the j values as subscripts following the m values, we have as q states, $4d_{01}$, $4d_{02}$, $4d_{03}$, and the amplitude of the transition considered is

$$A(4p_0,2p_0)=\frac{E}{2h}\frac{A(4d_{01},2p_{02})A(4d_{01},4p_{01})}{\nu(4d,4p)}(1+0+54) \tag{18}$$

The sum of the squares of the amplitudes of all the $2p-4p$ transitions gives

$$\frac{I^r(4p,2p)}{I^r(4d,2p)}=\frac{E^2}{4h^2}\frac{A(4p_{02},4d_{01})^2}{\nu(4d,4p)^2}\frac{4675}{9} \tag{19}$$

For comparison with the amplitudes obtained from the intensity measurements by calculations similar to the above, calculations were made of the amplitudes of corresponding amplitudes in hydrogen by the method of Schrödinger. This author has shown[17] that the *eigenfunktionen*

[17] Schrödinger, Ann. d. Physik **79**, 734 (1926).

given in an earlier paper[18] give the Heisenberg matrices and can therefore be used to calculate amplitudes exactly, without the uncertainties of the older methods. The formulas used are: His formula for the *eigenfunktionen* in his first paper,[18] formulas (5) and (6) in the paper discussing the relation between his quantum mechanics and the Heisenberg quantum mechanics.[17] Calculations were made for all amplitudes calculated from the dispersion theory and the intensity measurements, and also for the amplitudes needed to determine which terms must be included in formula (1) to give the desired approximation. The recent work of Heisenberg[19] on the helium spectrum shows that the amplitudes calculated for hydrogen will be correct for helium to a good approximation. The amplitudes calculated in this way follow, (they are all for $m'=0\rightarrow m''=0$).

Line:	$2P-4D$	$2P-4S$	$2P-5D$	$2P-5S$	$4P-4D$	$4D-4F$
Amplitude:	$1.8a_0$	$0.40a_0$	$1.0a_0$	$0.29a_0$	$21a_0$	$16a_0$

Line:	$4S-4P$	$5S-4P$	$5D-4P$	$5P-5D$	$5S-5P$
Amplitude:	$27a_0$	$9.1a_0$	$17a_0$	$35a_0$	$42a_0$

where a_0 is the amplitude of the smallest orbit in hydrogen, 0.532×10^{-8} cm.

In order to compare the amplitudes in parhelium with those in orthohelium and the latter with the calculated amplitudes it is convenient to introduce a "total" amplitude defined by the relation

$$I(p,q)=\frac{[2\pi\nu(p,q)]^4}{3c^3}a^2(p,q)3N(p) \tag{20}$$

where $N(p)$ is the total number of atoms in the state p. From any amplitude for specific values of m' and m'' this total amplitude is easily obtained by the Kronig rules.

Experimental Method

The method of Lo Surdo, in which the electric field of the cathode dark space produces the Stark effect was used. The tube was set with the surface of the cathode parallel to the slit of the spectrograph, so that the light falling on the slit was all from a portion of the tube in which the field intensity was approximately the same. A cathode of molybdenum, one-half centimeter in diameter, was used. This was enclosed in two quartz tubes fitting one over the other, the inner of which ended

[18] Schrödinger, Ann. d. Physik **79**, 361 (1926).
[19] Heisenberg, Zeits. f. Physik **38**, 421; **39**, 499 (1926).

at the surface of the cathode, while the outer tube extended about two centimeters further. A small slit was cut in the outer tube close to the surface of the cathode where the glow is brightest and the image of this slit focussed on the slit of the spectrograph. A double image prism was used to separate the parallel components of the lines from the perpendicular. Two direct current generators, each capable of supplying 4,000 volts, were used in series. The voltage supplied could be varied by varying the current through the magnets of the generator and was very constant. The helium used was purified by passing over charcoal at liquid air temperature, and a charcoal tube immersed in liquid air was always in the system when the discharge was passing. No impurity lines except the strongest lines of mercury, which appeared with low intensity, the carbon line at $\lambda = 4267$ and the Balmer lines showed on the plates. It was not found necessary to have the system of large volume when a charcoal tube immersed in liquid air was included in it. The tube usually ran so smoothly that there was no swinging of the needle of the voltmeter connected across it. A current of from 10 to 6 milliamperes with a voltage of from three to eight thousand volts was used, with exposures of from one to six hours. A plane grating spectrograph made in this laboratory and having a dispersion in the first order of 17 angstroms per millimeter was used. The blackening of the plate was measured in a Moll microphotometer of magnification about 100. The method of obtaining the intensities of the lines from the blackening of the plate was the following: The spectrum of a Phillips Argenta lamp was photographed with a constant current flowing through the lamp. A large number of exposures were taken, each two minutes long, with varying slit width. The blackening of the plate was then measured at a constant wave-length and varying slit width and the photographic density plotted against the logarithm of the slit width. The curve obtained was a straight line for all except very low blackenings. The lower, curved portion of the curve was plotted from a large number of points and appeared to give as accurate results as the straight line portion. Such curves were made for a number of wave-lengths over the range of wave-lengths used in this investigation. All curves were taken from more than one plate and points from different plates fell on the same curve with the same accuracy as did points from the same plate. Blackening curves of wave-lengths between four and five thousand were of the same form except for small differences in the curved portions but for wave-lengths shorter than four thousand the slope of the curve dropped off rapidly with decreasing wave-length. To determine the intensity of a line in the helium spectrum the blackening of the plate

was measured in the photometer and the slit width corresponding to this blackening was read off the curve taken for a wave-length near that of the line. (It is assumed that the intensity of the light falling on the plate is for a continuous spectrum proportional to the width of the slit of the spectrograph.) It is obvious that this method of comparing intensities does not allow the comparison of intensities of lines whose wave-lengths differ appreciably from each other, unless the distribution of energy with wave-length is known for the lamp used, which was not the case in this work. It is hoped later to determine the sensitivity of the plate to different wave-lengths so that lines of different wave-lengths may be compared. Ilford Special Rapid Chromatic plates were used. They were developed in one part rodinol to twenty parts water at 18°C for four minutes. Any desired slope may be obtained for the blackening curve by varying the time of development.

Where it was desired to compare the intensity of lines of very different intensities an exposure long enough to bring out the weak line with measureable intensity gave the strong line too greatly overexposed to measure its blackening. For this reason exposures of one-tenth and one-one-hundredth the time of exposure of the strong exposure were made. The blackening of as many lines as possible which could be measured on two exposures gave a value of the ratio of the intensities of the two exposures and from this ratio the intensity of the strong line on the strong exposure was calculated. Where the intensity of parallel and perpendicular lines is compared, the intensities of the exposures were compared by assuming that such lines as $2p-ms$, $2p-4d$, etc. were unpolarised. As these lines all gave the same value for the ratio of the intensity of the parallel to the intensity of the perpendicular exposure the assumption was justified by the results.

We cannot *a priori* expect the blackening curves to be of the same form for exposures of different lengths so that the procedure used here is open to obvious theoretical objections. The results show, however, that no large error was introduced by using blackening curves taken with two minute exposures to determine the intensity of lines in exposures of times up to six hours. Where a number of lines were measured in a two minute and in a twenty-five minute exposure and the ratio of the energy which had fallen on the plate during the two minute exposure to that which had fallen on the plate in the half hour exposure determined from each of these lines the values obtained from the different lines agreed fairly well with each other. The same thing was true for the twenty-five minute and four hour exposures. That is, the measured ratio of the different lines to each other was the same for a two minute,

a twenty-five minute and a four hour exposure. The largest a.d. obtained in measuring the ratio of the intensity of two exposures to each other was thirty percent and the a.d. was usually between ten and twenty percent. For the ratio of the intensity of the parallel to the intensity of the perpendicular exposures the agreement was in general better, even when values taken from exposures of different lengths but taken under the same conditions were averaged. Unless some compensation of errors takes place a systematic error in the measurements should also appear as a systematic change with field of the value of the intensity of a combination line divided by the square of the field.

Results

Measurements are given of the intensities of the groups of lines $2P-nM$ and $2p-nm$ for $n=4, 5, 6, 7$, $M=P, D, F, G$, etc. In addition the intensity of the combination lines $2S-4D$ and $2S-4F$ and the line $2S-4P$ have been measured. Table I gives the ratios of the intensities of the combination lines of parhelium to the nearest original line for all

TABLE I

The intensities of the combination lines of parhelium and the amplitudes calculable from them

Field	$\frac{I^r(4D,\ 2S)}{I^r(4P,\ 2S)}$	$\frac{I^r(4D,\ 2S)}{I^r(4D,\ 2P)} \div E^2\times 10^{10}$	$\frac{I^r(4F,\ 2S)}{I^r(4P,\ 2P)}$	$\frac{I^r(4F,\ 2S)}{I^r(4F,\ 2P)} \div E^4\times 10^{19}$	$\frac{I^r(4P,\ 2P)}{I^r(4D,\ 2P)}$	$\frac{I^r(4P,\ 2P)}{I^r(4D,\ 2P)} \div E^2\times 10^{10}$	$\frac{I^r(4F,\ 2P)}{I^r(4D,\ 2P)}$	$\frac{I^r(4F,\ 2P)}{I^r(4D,\ 2P)} \div E^2\times 10^{10}$	$\frac{I^r(5P,\ 2P)}{I^r(5D,\ 2P)}$	$\frac{I^r(5P,\ 2P)}{I^r(5D,\ 2P)} \div E^2\times 10^{10}$
Kv/cm		$\frac{cm^2}{v^2}$		$\frac{cm^4}{v^2}$		$\frac{cm^2}{v^2}$		$\frac{cm^2}{v^2}$		$\frac{cm^2}{v^2}$
13.2					.025*	1.4				
14.2	.026	1.3	.010	2.6	.031	1.6	.30	15	.16	8.0
16.2	.028	(1.1)	.021	3.1	.032	1.2	.36	14	.34	13.
18.6	.035	(1.0)	.33	2.8	.053	1.5	.55	16	.44	13.
19.8	.036	(.92)	.33	(2.1)	.053†	(1.3)	.54†	(14)	.49†	13.
24.3	.049	(.89)	.46	(1.6)						
Average				2.8		1.4		15		12
Amplitude (cm)	$a(4P,4D)$ 1.2×10^{-7}		$A(4P,4D)A(4D,4F)$ 8.0×10^{-15}		$a(4P,4D)$ 1.3×10^{-7}		$a(4D,4F)$ 5.1×10^{-8}		$a(5P,5D)$ 2.1×10^{-7}	
Calc. Amplitudes	1.1×10^{-7}		4.9×10^{-15}		1.1×10^{-7}		4.6×10^{-8}		1.7×10^{-7}	

*From the measurements of Takamine and Werner.
†At this and higher fields the D-line is probably double.
Values in parentheses were not used in calculating the amplitudes.

the combination lines measured which may be considered to be emitted in a weak field. Table II gives the same information for orthohelium. The amplitudes calculable from the measured ratios are given in both tables. It is seen at once from the tables that the measured agree approximately with the theoretical values of the amplitudes. The intensity of the combination lines divided by the square of the field shows no systematic variation except in the case of $2S-4D$. Since the $4D$ term

TABLE II

The intensities of the combination lines of orthohelium and the amplitudes calculable from them

Field	$\frac{I^{\pi}(4p,\ 2p)}{I^{\pi}(4d,\ 2p)}$	$\frac{I^{\pi}(4p,\ 2p)}{I^{\pi}(4d,\ 2p)} \div E^2 \times 10^{10}$	$\frac{I^{\pi}(4f,\ 2p)}{I^{\pi}(4d,\ 2p)}$	$\frac{I^{\pi}(4f,\ 2p)}{I^{\pi}(4d\ 2p)} \div E^2 \times 10^{10}$	$\frac{I^{\pi}(5p,\ 2p)}{I^{\pi}(5d,\ 2p)}$	$\frac{I^{\pi}(5p,\ 2p)}{I^{\pi}(5d,\ 2p)} \div E^2 \times 10^{10}$
Kv/cm		$\frac{\text{cm}^2}{\text{v}^2}$		$\frac{\text{cm}^2}{\text{v}^2}$		$\frac{\text{cm}^2}{\text{v}^2}$
13.2	.0015*	.086*				
14.2	.0017	.086	.16	.80	.026	1.3
16.2	.0023	.089	.17	.66	Hg line superposed	
18.6	.0028	.080	.20	.57	.043	1.2
19.8	.0031	.079	.25	.65	.040	1.0
24.3	.0049	.089	.34	.63	.12	(2.2)
Average		$.085 \pm .004$		$.66 \pm 0.05$		$1.2 \pm .1$
Amplitude (cm) Calc.		$a(4p, 4d)1.6\times10^{-7}$		$a(4d, 4p)6.2\times10^{-8}$		$a(5p,5d)3.1\times10^{-7}$
Amplitudes		1.1×10^{-7}		4.6×10^{-8}		1.7×10^{-7}

*From the measurements of Takamine and Werner.

lies very close to the $4F$ term this variation is not unexpected. The deviation of the measured ratios over the square of the field from the average values gives some idea of the experimental accuracy, at least for orthohelium where more measurements may be averaged. It is particularly satisfactory that the measurements made by Takamine and Werner agree with those given here for the $p-p$ lines. Their measurements of the $p-f$ lines are not included since they did not use sufficient dispersion to separate these lines from the $p-d$ lines.

The amplitudes of $4D-4P$, $4F-4D$ etc. calculated from these measurements show a systematic deviation from those calculated for hydrogen. More weight is to be attached to the values for $2D-4D$, $2p-4p$ and $2p-5p$ than to the others since the condition for a weak field is better fulfilled for these lines. It is seen that the amplitudes calculated from the intensities of these lines are consistently high. The agreement among the values themselves for parhelium is better, the amplitude $a(4P,\ 4D)$

calculated from the intensity of $2S-4D$ agreeing within fifteen percent with the amplitude $a(4P, 4D)$ calculated from the intensity of $2P-4D$ and the product $a(4P, 4D)\ a(4D, 4F)$ calculated from $2S-4F$ agreeing fairly well with the product calculated from the intensities of $2P-4P$ and $2P-4F$. It will at first be thought that the agreement could be improved by taking into account more terms in the formulas used in

TABLE III

The ratios of the intensities of the parallel components of the combination lines to perpendicular components

Parhelium

Field Kv/cm	$\frac{I^{\pi}(4P,\ 2P)}{I^{\sigma}(4P, 2P)}$	$\frac{I^{\pi}(5P,\ 2P)}{I^{\sigma}(5P, 2P)}$	$\frac{I^{\pi}(6P, 2P)}{I^{\sigma}(6P, 2P)}$	$\frac{I^{\pi}(7P, 2P)}{I^{\sigma}(7P, 2P)}$	$\frac{I^{\pi}(4D, 2S)}{I^{\sigma}(4D, 2S)}$	$\frac{I^{\pi}(4F, 2P)}{I^{\sigma}(4F, 2P)}$
14.2	2.9	2.6	2.5	2.4	1.3	1.1
16.2	2.5	1.8			1.1	1.4
18.6	2.5	2.6			1.4	1.2
19.8	2.6				1.6	(.95)
24.3	(3.3)				(2.1)	
Av.	2.6	2.3	2.5	2.4	1.3	1.2
Calc.	2.6	2.6	2.6	2.6	1.3	1.3

Orthohelium

Field Kv/cm	$\frac{I^{\pi}(4p,\ 2p)}{I^{\sigma}(4p, 2p)}$	$\frac{I^{\pi}(5p, 2p)}{I^{\sigma}(5p, 2p)}$	$\frac{I^{\pi}(6p, 2p)}{I\delta(6p, 2p)}$	$\frac{I^{\pi}(7p, 2p)}{I^{\sigma}(7p, 2p)}$	$\frac{I^{\pi}(4f, 2p)}{I^{\sigma}(4f, 2p)}$
14.2	2.0	2.0	2.0	2.5	1.5
16.2			2.4		1.2
18.6	1.7	1.9	2.2	2.6	1.6
19.8	1.6	1.7	2.6	1.5	1.5
24.3	1.5	1.7	1.6	1.8	
Av.	1.7	1.8	2.2	2.1	1.4

calculating the amplitudes, since the sum of a large number of small terms may become appreciable compared with one large term. Additional terms, however, will not all be of the same sign and will tend to cancel out. It is more likely that the disagreement is due almost entirely to experimental error, introduced from the source discussed in the last section or in other ways. It is unlikely that the experimental error is larger than forty percent, but it may be as large as this, at least where lines of very different intensities are compared. The comparison of lines of nearly the same intensity and of the same wave-length is considerably more accurate. (Compare, for instance, the agreement shown by the values given in Table III with the agreement shown by the values in the first two tables.) It is possible that the large disagreement shown for $a(4p-4d)$ is connected with the fact that the frequencies of the lines

$2p-4p$ and $2p-4d$ differ by more than do the frequencies of any other pair of lines of which the intensities have been compared.

In Table III the ratios of the intensity of the parallel components of the combination lines to the perpendicular components of the lines are given, together with the calculated value of this ratio. The agreement between measured and calculated values is better than is to be expected, even lines which must be considered to be emitted in a very high field such as $2p-2p$ giving approximately the calculated ratio. The ratios for the triplet system do not seem to approach those for the

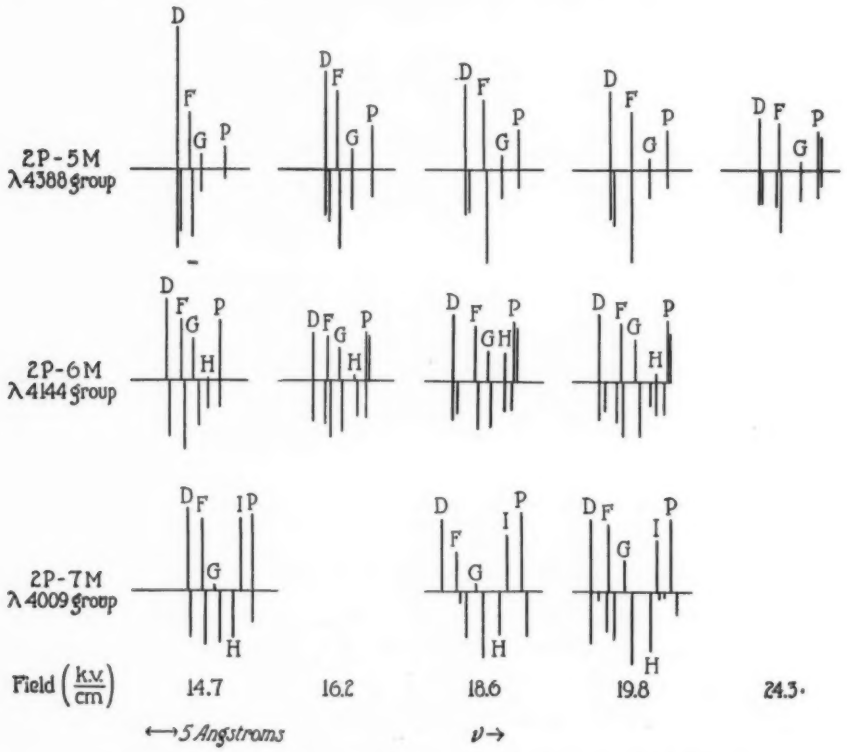

Fig. 4. The relative intensities of parhelium lines in various fields.

singlet system as the field increases, as would be expected from analogy with the Zeeman effect. The ratios not given in the table are of lines believed to be unresolved doublets or of lines too weak to measure. All the measurements on parhelium lines of principal quantum number higher than four are affected by insufficient resolution.

In Figs. 4 and 5 the results of the measurements on $2P-nM$ and $2P-nm$ are given for $n=5$, 6 and 7. The length of the lines represents

the intensities, the unit being arbitrarily chosen so that the sum of the intensities of all lines in one group is the same for different fields and different groups of lines. It is therefore only possible to use the figures for comparison within one group. The parallel and perpendicular lines are reduced to the same units, and the parallel lines represented by lines above and the perpendicular ones by lines below the base line. The

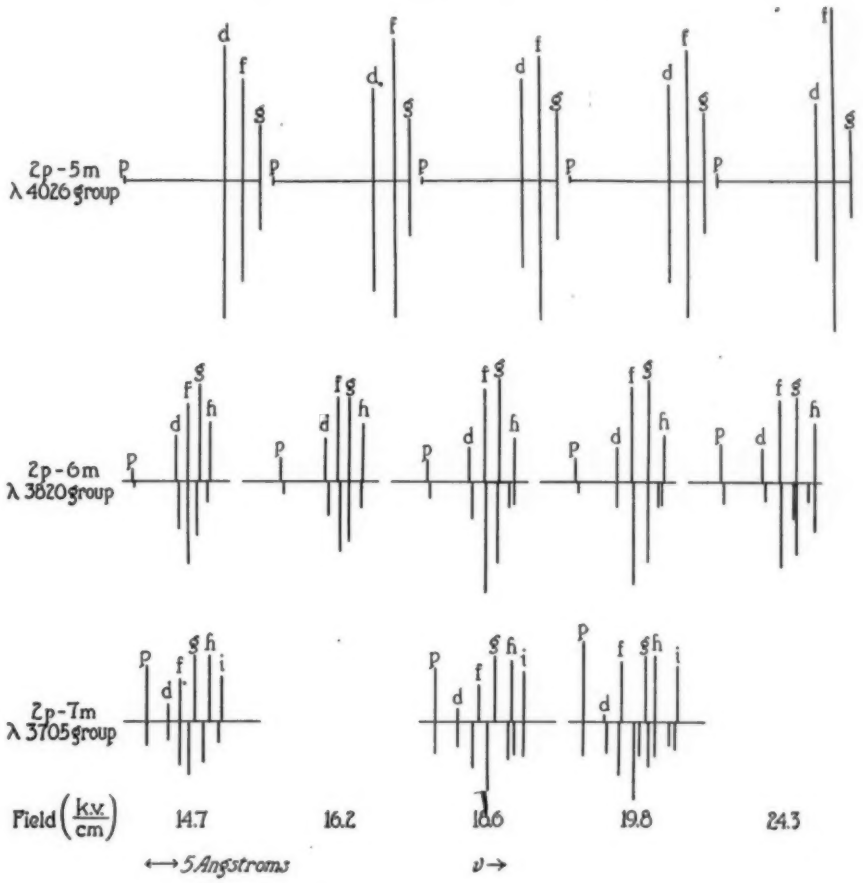

Fig. 5. The relative intensities of orthohelium lines in various fields.

groups omitted were too weak to measure. More weight is to be given Fig. 4 than Fig. 5, because of the error in the parhelium lines just referred to. When a doublet is only partially separated the measured intensity lies between the sum of the intensities of the two lines composing it and the intensity of the strongest line of the doublet. The results show an increasing resemblance between the hydrogen and the helium Stark

effect as we increase the field or go to lines of higher quantum number. It does not seem possible to find a detailed connection between the intensities in hydrogen and helium, however. In general the lines which are weak in hydrogen in strong fields are those which diminish in intensity with increasing field in helium, but the rate of decrease does not seem to be that to be expected from comparison with hydrogen. Nor do parhelium and orthohelium resemble each other closely. A striking example of this is that the *d* lines disappear very much more rapidly in orthohelium than in parhelium although parhelium, because of the smaller separation of its terms must be considered to be emitting in the stronger field.

The experiments reported here were carried out in the University Institute for Theoretical Physics in Copenhagen. The author wishes to express her thanks to Professor Niels Bohr for the suggestion of the problem and for his interest and advice throughout the work, to Mr. Sven Werner for placing at her disposal the results of his experience in the same work, and to Professor Kramers and Dr. Heisenberg for valuable assistance in handling the theory. To the undergraduates of Barnard College are due her best thanks for the award of the fellowship which made her stay in Copenhagen possible.

UNIVERSITETETS INSTITUT FOR TEORETISK FYSIK,
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VOLTAGE-INTENSITY RELATIONS OF MERCURY LINES BELOW IONIZATION

By D. R. White

Abstract

Accelerating voltage-intensity relations have been obtained for twenty-eight lines of the mercury spectrum (between 5500A and 2500A) excited by electronic bombardment at potentials less than the ionization potential. The tube in which the radiation was excited had four electrodes, hot cathode and three grids, and the observations were made by photographic spectrophotometric measurements. In agreement with the results of other workers, the minimum potential of excitation of a line is found to agree closely with the theoretical value in all cases but one. The curves representing the voltage-intensity relation for lines with a common outer orbit are found identical when the intensity scales are so chosen as to arbitrarily make the curves coincide at one point. Upward and downward breaks are found in these curves at certain critical potentials but the character of the breaks and the potentials at which they occur change from series to series. The *ratio of the numbers of quanta emitted* in the lines of the triplet $2p_1-2s(5461)$, $2p_2-2s(4358)$, $2p_3-2s(4047)$ with an accelerating voltage of 10.2 volts was found to be 9 : 11 : 3.

Introduction

IT HAS been shown by Eldridge,[1] Hertz,[2] Hughes and Hagenow,[3] and Newman,[4] that it is possible to excite in stages the arc spectrum of each of a number of elements. This group by group excitation is simply explained by the Bohr theory. Each group of lines is found to contain only lines having a common outer orbit and the number of lines, then, in any group depends upon the number of transitions corresponding to emission of radiation which begin at that orbit. Such transitions may take the valence electron to its normal orbit in one step or they may be the first of a series of transitions which carries the valence electron to its normal orbit. Each of these groups was found to be present only when the energy of the bombarding electrons was greater than the minimum necessary for a single impact to raise the valence electron from its normal orbit to the outer orbit which was common to the group of lines.

Hertz and de Visser[5] went farther than this and investigated in detail the relation between the voltage of excitation and the intensity of light

[1] J. A. Eldridge, Phys. Rev. **23**, 685 (1924).
[2] G. Hertz, Zeits. f. Physik **22**, 18 (1924).
[3] A. Ll. Hughes and C. F. Hagenow, Phys. Rev. **24**, 229 (1924).
[4] F. H. Newman, Phil. Mag. **50**, 165, 796 and 1276 (1925).
[5] G. Hertz and J. C. Scharp de Visser, Zeits. f. Physik **31**, 470 (1925).

emitted for a few of the lines of helium and neon. They studied two helium lines and four neon lines which lie in the visible region of the spectrum. In the case of mercury we have found it possible to push this type of investigation further by use of a tube which gave a greater intensity of light than appears to have been previously obtained. Voltage-intensity curves are presented here for twenty-eight lines of the mercury spectrum lying in the region 5500A to 2500A.

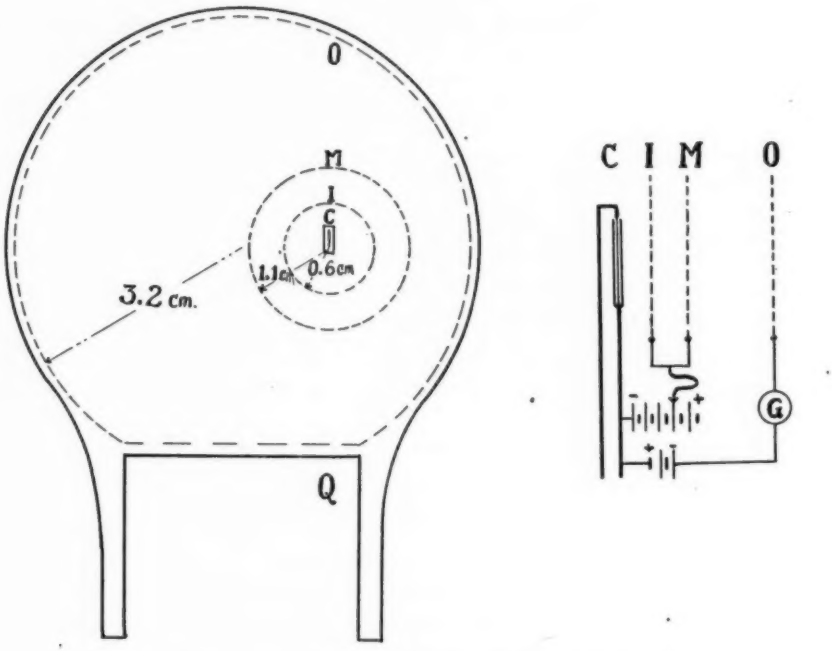

Fig. 1. Cross section of the experimental tube and the essential electrical circuits.

Apparatus and Experimental Details

A cylindrical tube, about 6.5 cm in diameter and 20 cm long was used for this investigation. A horizontal section of it is shown in Fig. 1 with the grid diameters indicated. The equipotential oxide coated platinum cathode[6] *C* was 4 mm wide by 37 mm long and was surrounded by two cylindrical grids *I* and *M* as shown. These grids were made of nickel gauze, 7 meshes per centimeter and wires 0.29 mm in diameter. They extended at both ends about 30 mm beyond the cathode and were supported on the glass arm that carried the leads to the cathode. A variable voltage was applied to these by means of the batteries indicated. The

[6] The cathode was similar to that described by Harold W. Webb, Phys. Rev. **24**, 116 (1924).

grid O, also of nickel gauze, lined the walls of the tube, and was kept at a potential of -3 volts with respect to the cathode for most of the experiments and had in its circuit a galvanometer G which measured the current to it. The reentrant quartz window Q permitted spectroscopic study of the radiation produced within the tube.

The gas was removed from the tube by continuously operated pumps connected near its top which kept the residual gas pressure less than 5×10^{-5} mm. At the same time the supply of mercury vapor was maintained by evaporation from a drop of mercury at the bottom of the tube

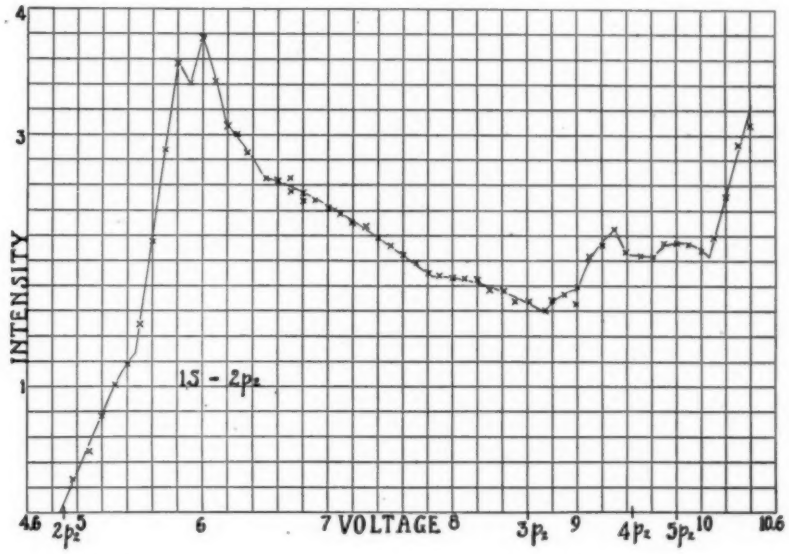

Fig. 2. Accelerating voltage-intensity relation for the line $1S-2p_2(2537)$.

which was heated by an electric heater. No accurate estimate of the mercury vapor pressure can be given for these conditions as evaporation was taking place at approximately 230°C and condensation at approximately 40°C. However an accurate estimate of the vapor pressure is of no particular importance as the results were not found to change materially for evaporation temperatures varying between 210°C and 250°C.

The spectroscopic observations were made with a small quartz spectrograph which gave a dispersion of 7A per millimeter in the region of 2500A. In the region of 3600A the dispersion was less so that, when the slit was opened sufficiently to give line widths great enough for satisfactory density measurements, the lines overlapped in each of the groups[7] $2p_1-mD$, $2p_1-md_{123}$; $2p_2-mD$, $2p_2-md_{23}$; and $2p_3-mD$, $2p-md_3$.

[7] Paschen-Gotze, Seriengesetze der Linienspektren, p. 116 (1922).

(For brevity these groups of lines will be designated as $2p_1-mDd_{123}$, $2p_2-mDd_{23}$ and $2p_3-mDd_3$ respectively.)

The densities were measured by means of a densitometer in which the relative intensity of the light transmitted by a small portion of the plate was measured by a photo-electric cell kindly furnished us by Dr. H. E. Ives. The photo-electric current was measured by balancing its Ir drop in a resistance of 20 megohms by a direct reading potentiometer. Both were placed in the grid circuit of a radio vacuum tube in such a manner that at the point of balance the plate current was unchanged as the

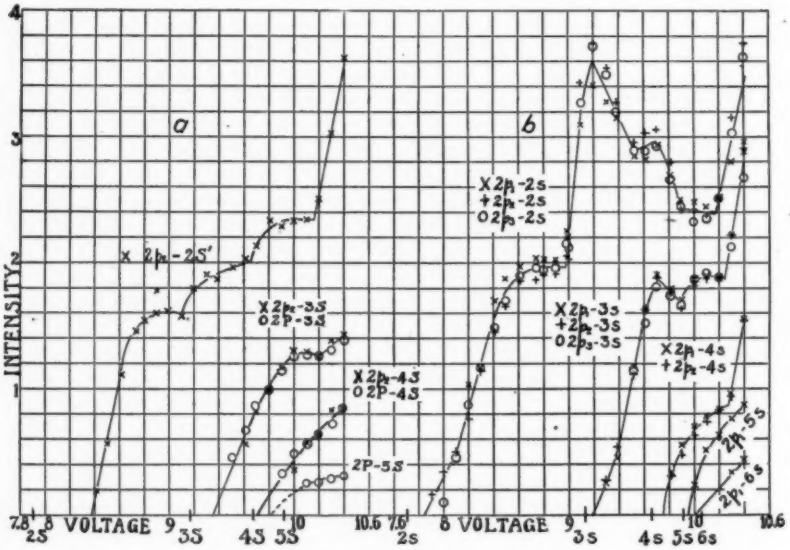

Fig. 3. Accelerating voltage-intensity relations for lines with S and s orbits as outer ones.

potentiometer and resistance were switched into and out of the grid circuit. A circuit, similar to that of a simple potentiometer, connected in the plate circuit of the vacuum tube made it possible for a galvanometer to detect smaller changes of current than could a meter capable of carrying the entire plate current. This arrangement was found necessary to attain the precision desired.

When the tube was operated, electrons came from the grounded cathode C, were accelerated in the space between C and I and then were allowed to move freely in the space between I and M which was kept free from externally applied fields by directly connecting M to I. Upon entering the space between M and O the electrons were slowed down and were then returned to either M or I by the negative potential on O. Under these conditions it was observed that the radiation was excited

in a space represented by a hollow cylinder having the grid I for its inner surface and an outer diameter some 5 mm greater than the diameter of M. This volume, in which the radiation originated, remained approximately constant for voltages more than half a volt below the ionization potential but increased rapidly for higher voltages and entirely filled the tube at the ionization potential.

The theoretical value for the ionization potential is 10.4 volts but it was found to be an applied accelerating potential varying from week to week between the limits 11.6 and 12.0 volts. The difference, which was

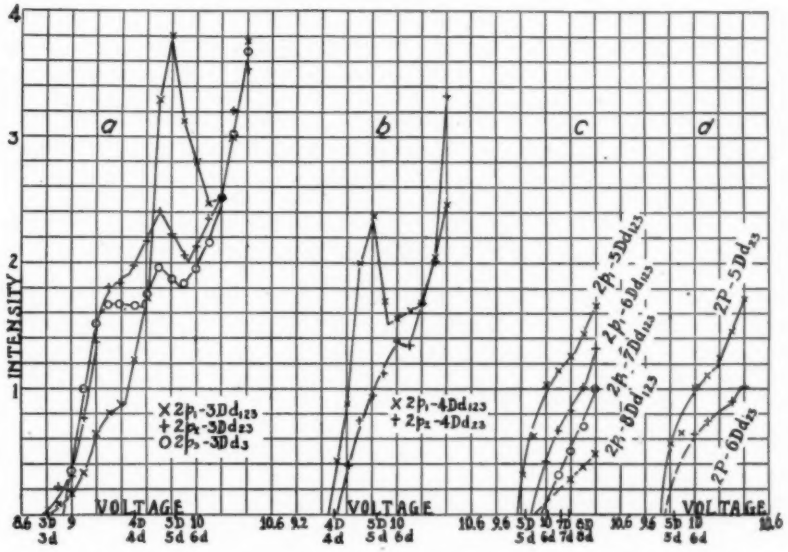

Fig. 4. Accelerating voltage-intensity relations for lines with D and d_{123} orbits as outer ones. Groups of lines for which the frequency difference is due to energy differences of the D and d_{123} orbits were not separated with the spectrograph used.

the voltage correction subtracted from all the accelerating voltage readings of any series, was due to a 0.2 volt drop in the leads and a variable correction due to contact difference of potential and the initial velocity of the electrons from the cathode. The ionization potential was determined by means of the galvanometer G in the circuit of the grid O. Since this grid was at a sufficiently great negative potential with respect to the cathode to keep electrons from reaching it, the current from it, through the galvanometer, must have been due to leakage across the insulation and to positive ions. An accelerating voltage-galvanometer current curve for the second of these components should show a very great increase of slope when the speed of the electrons is such that a

single impact can just ionize an atom, while the first component should not show any such characteristic. The accelerating voltage corresponding to this abrupt increase of slope was taken as the ionization point.

Results

The results of the investigation are presented in the typical accelerating voltage-intensity curves Figs. 2, 3 and 4. The curves are grouped according to the outer orbit of the transition. Fig. 2 shows the curve for the transition $1S-2p_2$. Fig. 3 shows curves for transitions with ms and mS as outer orbits. Fig. 4 gives the curves for transitions $2p_i-mDd_{123}$. Table I lists the lines observed and gives an approximate idea of their relative strengths. The first column gives the notation for the transition, the second gives the wave-length, the third gives the symbol used to designate the points on the curve and the fourth gives the photographic density for an accelerating potential of 10.2 volts and hence an approximate idea of the relative strength of each line.

TABLE I

The lines observed and their photographic density at 10.2 volts

Notation	λ	Symbol	Density	Notation	λ	Symbol	Density
	Fig 2				Fig 4(a)		
$1S-2p_2$	2537	×	1.24	$2p_1-3Dd_{123}$	3650	×	1.70
	Fig 3(a)			$2p_2-3Dd_{23}$	3125	+	1.34
$2p_2-2S$	4078	×	.72	$2p_3-3Dd_3$	2967	○	.72
$2p_2-3S$	2858	×	.10		Fig 4(b)		
$2P-3S$	4916	○	.32	$2p_1-4Dd_{123}$	3025	×	.69
$2p_2-4S$	2563	×	.03	$2p_2-4Dd_{23}$	2652	+	.56
$2P-4S$	4108	○	.34	$2p_1-5Dd_{123}$	2803	×	.30
$2P-5S$	3801	○	.02	$2p_1-6Dd_{123}$	2698	+	.11
	Fig 3(b)			$2p_1-7Dd_{123}$	2639	○	.03
$2p_1-2s$	5461	×	.80	$2p_1-8Dd_{123}$	2603	×	.01
$2p_2-2s$	4358	+	1.48		Fig 4(d)		
$2p_3-2s$	4047	○	1.11	$2P-5Dd_{23}$	3906	×	.15
				$2P-5Dd_{23}$	3704	+	.03
$2p_1-3s$	3341	×	.52				
$2p_2-3s$	2893	+	.44				
$2p_3-3s$	2752	○	.18				
$2p_1-4s$	2925	×	.22				
$2p_2-4s$	2576	+	.18				
$2p_1-5s$	2759	×	.05				
$2p_1-6s$	2674	×	.01*				

*Density at 10.3 volts.

For all curves obtained in these experiments, spectrograms were made in order of increasing voltage at approximately 0.1 or 0.2 volt intervals. As more than one plate was needed in a series of spectrograms, exposures at two voltages were repeated on the second plate to insure continuity.

In addition, on each plate used, there was at least one group of three spectrograms for which the tube was held constant while the intensity was varied in known ratios by screens in the optical system of the spectrograph. The density-intensity relation thus obtained for any line was graphically extrapolated when necessary to obtain the complete voltage-intensity relationship for the line.

The corrected voltages are in all cases the abscissas of the curves. The correction used is known to only $\pm .05$ volt and hence all potentials are in doubt by that amount although the differences of potential between the points are known to $\pm .02$ volt. The ordinates are the intensities per milli-ampere emission and were obtained by dividing the intensity found from the photographic plates by the emission from the cathode when the spectrogram was taken. These ordinates have a precision of about 4 percent for most of the points though the accuracy is less at the lowest and the highest intensities of the lines.

A value of the minimum potential necessary for the excitation of the different lines was obtained by extrapolating the voltage-intensity curves to the voltage axis. The intercept thus found is the minimum value of the accelerating potential for excitation of the lines. This intercept agrees with the theoretical value, which is noted on the voltage axis of the curve, within the limit of accuracy of the extrapolation, in accordance with the conclusions of Eldridge and Hertz, for all lines but one. In the case of the transition $2p_2-2S$, $\lambda 4078$, the intercept is 8.3 volts while the theoretical value is 7.9 volts. It is possible that there is another break in the curve at an intensity below the limit of sensitivity of the method that would carry the curve to 7.9 volts.

In all cases where two or more lines had the same outer orbit, the curves representing the voltage-intensity relation were identical when the intensity scales were so chosen that the curves coincided at one point. This is shown in Fig. 3. Fig. 3(*b*) shows curves for the groups of lines $2p_i-2s$, $2p_i-3s$ and $2p_i-4s$ which have the common outer orbits $2s$, $3s$ and $4s$ respectively. The observed intensities, arbitrarily plotted as equal at 10.2 volts, are indicated by the symbols in the figure. Only one curve was drawn as that represents all points within the experimental error. In a similar manner the pairs of lines $2P-3S$, $2p_2-3S$; and $2P-4S$, $2p_2-4S$ are plotted in Fig. 3(a). The same close agreement between the curves is observed. This is of particular importance as each pair has one line belonging to the singlet series and one to the combination series.

The information obtained concerning the lines with D and d orbits as outer orbits is not sufficient to determine whether or not the same sort of similarity holds there also. This is due to the fact that the spectrograph did not separate completely groups of the type $2p-mDd_{123}$ since the multiplicity is due to the D and d_{123} levels which have small energy differences.

The result found in the cases of the ms and mS orbits leads to the conclusion that the ratio of the number of quanta corresponding to the transitions of the types $x-mz$, and $y-mz$ ($z=s$ or S) is independent of the voltage of excitation. This is equivalent to the statement that the voltage of excitation does not affect the relative probability that an electron in one of these outer orbits will take anyone of the possible paths from that orbit. This has been shown to hold for s and S orbits and may hold more generally.

The ratio of the number of quanta corresponding to each of the transitions $2p_1-2s$, $2p_2-2s$ and $2p_3-2s$, wave-lengths 5461, 4358 and 4047A respectively, was determined. Such a ratio of quanta is evidently also the ratio of the probabilities of the different transitions. Similar determinations were attempted for ratios of quanta for other groups of lines but, owing to experimental difficulties, were unsuccessful.

For the ratio measured, a vacuum type mazda lamp, operated at a color temperature 2420°K was used as the comparison source of known energy distribution for the spectrophotometric measurements since all three lines lie in the region of the spectrum but slightly absorbed by the glass of the lamp. The energy ratio for the lines 5461 and 4358 was determined by visual spectrophotometric comparison and a similar ratio for the lines 4358 and 4047 was measured photographically. After multiplying each energy ratio by the ratio of the wave-lengths to reduce to the ratio of the number of quanta, the latter was found to be

$$Q_{5461} : Q_{4358} : Q_{4047} = 255 : 300 : 82$$
$$= 9 : 11 : 3$$

within 5 percent the accuracy of the experiment. The measurements were made with an accelerating potential of 10.2 volts applied to the tube, but as already pointed out, this ratio was found to be independent of the voltage. Coblentz[8] finds for the ratio of energy of these lines in the arc the value 4 : 2 : 1.

The intensity variations of the lines as the accelerating potential passes through critical potentials is of considerable interest. The following discussion will be limited to potentials less than about 9.8 volts as the

[8] Coblentz, Long and Kahler, Bull. Bur. of Standards **15**, 1 (1919).

series terms are separated so little at higher voltages that the voltage change of 0.1 or 0.2 volt between spectrograms does not accurately show detail.

Fig. 3(b) shows that lines with an s orbit as the outer one have maxima at the minimum excitation potentials of succeeding s terms. That is, the probability of excitation of a term of the series shows a rapid increase starting 0.1 or 0.2 volt below the minimum excitation potential of a higher term of the series and marked decrease starting at that potential. Such character is very definitely shown by the curves for $2p_i-2s$ and $2p_i-3s$ in the region of the minimum excitation potentials of $3s$, $4s$ and $4s$ respectively.

In contrast with this behavior, Fig. 3(a) shows the curve representing the transition $2p_2-2S$ with upward breaks at the minimum excitation potentials of $3S$ and $4S$ terms. However, there are no breaks in the curves for $2P-3S$ and $2p_2-3S$ at the excitation potential of $4S$. The data indicate that such a break should have been found if present to an extent comparable with the breaks in the $2p_2-2S$ curve.

The curves in Fig. 4(a) representing transitions $2p_1-3Dd_{123}$, $2p_2-3Dd_{23}$ and $2p_3-3Dd_3$ show upward breaks at approximately the minimum excitation potentials of higher terms of the series. Only a very general resemblance can be expected in these curves since because of the small dispersion of the spectrograph they represent the result of superposing two or more lines, and the d orbits involved in the lines superposed are different for the different $2p$ orbits. The lines superposed, as indicated previously, are $2p_1-mD$, $2p_1-md_{123}$; $2p_2-mD$, $2p_2-md_{23}$; and $2p_3-mD$, $2p_3-md_3$.

The curves for the transitions $2p_1-4Dd_{123}$ and $2p_2-4Dd_{23}$ are shown in Fig. 4(b) and are markedly dissimilar. They show much less similarity than found in the case of the transitions previously mentioned, those from $3D$ and $3d_{123}$. Even the points of maxima and minima do not occur at the same voltages in the two curves.

The accelerating voltage-intensity relation for the resonance line $1S-2p_2$, (2537) was also determined. In the curve representing this relation, Fig. 2, there is an upward break between 5.4 and 5.5. volts which is believed to be due to the excitation of metastable atoms in the $2p_1$ state which pass over to atoms in the $2p_2$ state as a result of impacts of the second kind.[9] The downward break which is found at 5.8 volts corresponds most closely to the excitation of the molecular band theoretically occurring at 5.7 volts. The upward break coming at 5.9 volts

[9] Klein and Rosseland, Zeits. f. Physik **4**, 46 (1921).

need not be interpreted as evidence of any new form of excitation, but only that a saturation value has been reached for the excitation of the molecular band. This is suggested by the fact that the slope of the line joining the points at 5.9 and 6.0 volts is approximately the same as the slope below 5.8 volts. There is a very marked downward break at 6.0 volts. This is a potential at which Miss Messenger[10] has shown that there is a rapid increase in the production of metastable atoms and hence this break is believed to be due to some form of excitation which produces little radiation but many metastable atoms. The general downward trend of the curve which started at the 6.0 volt break continues as far as 8.7 volts but in this interval there are three rather weak upward breaks. The significance of the first two of these, at 6.2 volts and 6.5 volts, respectively, is not clear. It is worthy of note that Miss Messenger[10] found a point of increased formation of metastable atoms at 6.3 volts and it is possible that this is to be identified with one of these breaks just mentioned. The third of these upward breaks occurs at 7.8 volts and is believed to be due to the presence of transitions from $2s$ to $2p$ at potentials above this value. The upward break at 8.7 volts marks the end of the general downward trend and the beginning of an upward slope which continues to 9.3 volts where there is a downward break. The upward break at 10.0 volts marks the beginning of an upward slope which continues to the highest potentials used. The 8.7 volt break is probably due to returns to $2p_2$ from $3D$ and $3d_{23}$ although the theoretical minimum excitation potential for these orbits is 8.8 volts. Since the $3p_2$ orbit has an excitation potential of 8.6 volts, this upward break at 8.7 volts might be interpreted as indicating for the $1S-2p_2$ transition a behavior similar to that found for the $2p_2-2S$ transition which had an upward break at the minimum excitation potentials of upper terms of the series. Thus it is seen that it is possible that this 8.7 break is the result of more than one cause. At 9.0 volts there is an upward break in the curve which is believed to be due to the rapid increase in the excitation of $2s$ starting at this potential (See Fig. 3(b)) which thereby increases returns from $2s$ to $2p_2$ and hence increases emission of $1S-2p_2$. The interpretation of the breaks at the higher potentials is not possible as transitions from so many orbits above 9 volts lead to $2p_2$ that it is no longer possible to determine the cause of any given break.

In considering the characteristics of these curves no reference has been made to double impacts of atoms and electrons as such impacts were found to be relatively improbable. If double impacts had been present

[10] Miss H. A. Messenger, Phys. Rev. **28**, 962 (1926).

two effects would have been noted. First, there would have been an appreciable positive ion current to grid *O* at potentials below the ionization point. No such positive ion current was shown by the galvanometer *G* and there was no spectroscopic evidence of ionization. Second, if double impacts had been relatively probable, upward breaks at both 9.6 and 9.8 volts in the curve $1S-2p_2$ would be expected, the first due to excitation of $2p_1$ and $2p_2$ successively by an electron and the second due to successive $2p_2$ excitation. A small break at 9.6 is observed but none whatever at 9.8 volts. In view of these two tests, it is evident that double impacts produced no appreciable effect in these experiments.

In conclusion, I thank Professor Harold W. Webb, at whose suggestion the work was undertaken, for his continued interest and guidance in the work. I also thank Professor H. W. Farwell for his encouragement and the laboratory facilities which he placed at my disposal.

PHOENIX PHYSICAL LABORATORIES,
COLUMBIA UNIVERSITY,
August 13, 1926.

THE EFFECTS OF CHANGES IN POTENTIAL AND FREQUENCY ON THE LINE SPECTRUM OF CERTAIN GASES

By James A. Swindler

Abstract

Using a Hilger quartz spectrograph, size C, spectrograms were made from electrodeless tubes containing helium, hydrogen, nitrogen, neon, xenon, krypton, mercury and chlorine. High frequency peak voltages were computed from the equation $E=KI\sqrt{d\lambda/C}$, where K is a constant depending upon the velocity of light and the cycles per second of the generator. An electroscope was constructed and calibrated for measuring the potential over the secondary of a 25000 volt transformer. Increasing the potential over the tube for either the 60 cycle or high frequency currents seemed merely to intensify the lines. Changes in frequency from 0.58×10^6 to 1.91×10^6 produced no changes in spectra. When the potential was kept approximately constant, marked differences were obtained, however, between the 60 cycle spectra and the high frequency spectra (1) of a chlorine tube containing nitrogen as an impurity, (2) of a helium tube containing nitrogen as an impurity and (3) of a helium tube containing mercury as an impurity.

SEVERAL experimenters[1,2] have called attention to differences that have occurred in line spectra as a result of the manner in which the luminosity of the gas has been excited. When such excitation is produced by high frequency currents it is claimed that the nature of the spectrum depends upon the capacity, the inductance and the potential of the oscillating circuit. It is also claimed that such a spectrum is modified greatly by changes in the pressure and temperature[3] of the gas. Since changes in inductance or capacity are, in most cases associated with changes in frequency, it would be interesting to know what part, if any, frequency plays in the production of spectra.

In order to make a study of the latter problem, E. O. Hulburt[4] compared the spectra obtained from an oscillating tube circuit capable of variations in frequency ranging from 3×10^6 to 0.43×10^7 cycles per second with that obtained from a 25000 volt transformer actuated by a

[1] Merton, Proc. Roy. Soc. **A89**, 447 (1912); Twyman, Wave-length Tables, Adam Hilger, Ltd., London; McVicker, Marsh and Stewart, J. Chem. Soc. (England) **124**, 642 (1923).

[2] Foley, Proc. Ind. Acad. Sci. **34**, 185 (1924).

[3] Robertson, Phys. Rev. **19**, 470 (1922); Wachsmith and Winawer, Ann. d. Physik **42**, 585 (1913); Dunoyer, Comptes Rendus **173**, 350 (1921); J. de Physique et le Radium **3**, 261 (1922).

[4] Hulburt, Phys. Rev. **20**, 127 (1922).

60 cycle alternating current and failed to find any differences in spectra resulting from the employment of different exciting frequencies. Since it is known, however, that high frequency spectra[5] do differ from those obtained by other methods of excitation, a further study of the problem seemed worth while. It is the object of this investigation, therefore, to determine, if possible, what effect changes in frequency or changes in potential have upon the spectrum of a gas at low pressure.

In the present investigation the spectrum of helium, hydrogen, nitrogen, neon, xenon, krypton, mercury and chlorine were studied. Most of the tubes were of the electrodeless dumbbell type, 12 cm in length with cylindrical bulbs 2 cm in diameter and 4 cm in length having inner diameters of approximately one-half millimeter. These tubes were pumped, filled and sealed by the late Sir William Ramsey, being a portion of the six dozen used by Dr. A. L. Foley[2] in his investigation on the stability of matter. There were equal numbers of glass and of quartz tubes in the allotment. In addition to these, eight tubes were purchased from the Hilton-Davis Company of Cincinnati, Ohio. These tubes were all electrode tubes, but were used as electrodeless tubes in all cases, by coating the outside terminals heavily with paraffine and then wrapping tin foil around each bulb.

A Hilger quartz spectrograph, size C, was used, giving a photograph 20 cm in length between λ2100 and λ8000. Near λ6000 this instrument is capable of resolving lines differing in wave-length by approximately 2A, while in the neighborhood of λ3000 the resolution is increased to differences of 0.12A. A cylindrical quartz lens was used in focusing light from the capillary of the tube upon the slit.

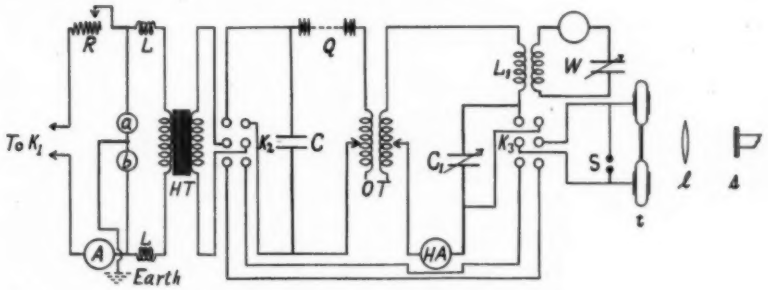

Fig. 1. Diagram of electrical connections.

Fig. 1 is a diagram of the oscillating circuit used in this investigation. The primary of a one kilowatt, 25000 volt transformer *HT* was subjected to a 60 cycle alternating current led in through K_1. The current through

[5] McVicker, Marsh and Stewart, loc. cit.

the ammeter A was controlled by the adjustable resistance R. The choke coils LL, grounded through the lamps a and b, were used to damp out any high frequency waves which might be carried over from the oscillating circuit. C was a two gallon Leyden jar having a capacity of 0.00124 microfarads. The oscillating transformer OT was a pancake coil consisting of about five turns on the primary and ten turns on the secondary. In series with each of these coils, tuning coils of heavy copper wire were inserted. The capacity C in some cases was a small Leyden jar of 0.000533 microfarad capacity, in other cases an adjustable oil condenser of similar average capacity. The current through the hot wire ammeter HA varied from 200 to 2000 milli-amperes depending upon conditions of the tube and circuit. The coil L_1 set up at approximately five feet from the oscillating circuit, consisted of two turns of wire. The diameter of these turns was about 10 cm. The wave meter W, which was found not to be in error by more than three percent of the correct wave-length, was used in measuring the frequencies of the oscillating circuits.

The order of procedure was as follows: After the circuit had been approximately adjusted to the wave-length desired, the coupling having been arranged to give the desired intensity, the ammeters A and HA were read and the wave-length and the decrement of the oscillation transformer secondary circuit recorded. The scale was first photographed, then the copper reference spectrum and then the tube spectrum. While making an exposure of the tube the slit was lengthened three times. This made possible the comparison of the intensities of lines having the same or different lengths of exposure. The total exposure varied from fifteen minutes in case of some of the tubes to as much as two hours in the case of others. The above procedure was repeated for one or two other frequencies. Then by use of switches K_2 and K_3 a sixty cycle frequency direct from the transformer was impressed upon the tube.

Theory of High Voltage Determinations

In the earlier part of this investigation a spark gap S, placed parallel with the tube, gave an estimation of the potential across its terminals; later this potential was computed in the following manner.

Voltage determination at high frequency. At the moment the discharge over the terminals of the condenser begins, letting I_0 be the initial current amplitude, E_0 the initial voltage over the condenser terminals, C the capacity and ω the frequency factor $2\pi n$, we have

$$I_0 = \omega C E_0. \tag{1}$$

Assuming that all the energy of each train of waves is dissipated before the next one begins, letting T be the period of a train of waves, in this

case 1/120 of a second, W_1 the energy dissipated in each train, then, since these two energies must be equal

$$RI^2T=\tfrac{1}{2}LI_0^2\,, \tag{2}$$

where L is the inductance of the circuit. Since d the decrement of a damped wave may be written $d=Rt/2L$, solving for R/L and substituting in the above equation gives

$$I_0^2=4dTI^2/t \tag{3}$$

Writing t in terms of λ, the wave-length, and combining Eqs. (1) and (3) gives, providing C is kept constant

$$E_0=KI\sqrt{d\lambda}. \tag{4}$$

In Eq. (4) K then becomes $(1/\pi C)\sqrt{T/V}$, where V is the velocity of the electric waves.

The decrement of the wave-meter was determined by the ordinary method[6] of reducing the root-mean-square value of the current to one-

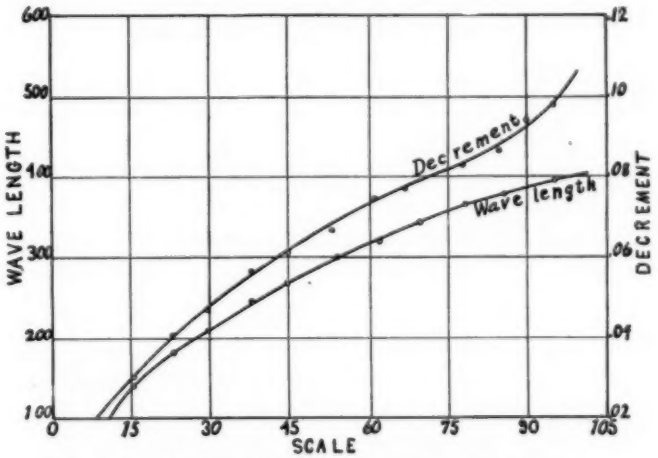

Fig. 2. Calibration curves for wavemeter and decremeter.

half value. In doing this two values of the capacity were found, one on either side of the resonance value. Under conditions of loose coupling the decrement is then given by the equation

$$d_1+d_2=\pi(C_2-C_1)/(C_2+C_1)\,,$$

where d_2 is the decrement of the wave-meter and d_1 the decrement of the sending circuit. If the wave-meter is tuned to a continuous wave sending circuit, d_2 is obtained directly. As the decrement of the wave-meter

[6] Ramsey, Proc. Ind. Acad. Sci. for 1922, pp. 223–226.

was found to vary with the frequency, curves were plotted showing the relation between decrement and wave-length for the coils used. With d_2 known the above equation gave the values of the decrement of the tube circuit.

When the capacity was kept constant and the inductance varied,the potential over the terminals of the condenser remained practically constant, providing the current through the hot wire ammeter was not altered. A number of photographs were taken in which a high frequency spectrum at resonance under moderately close coupling could be com-

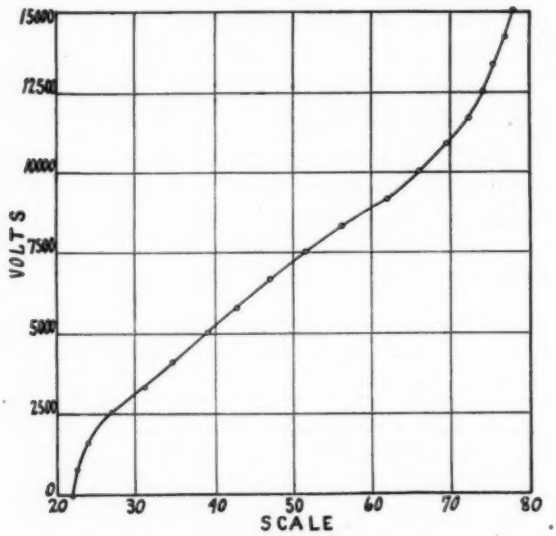

Fig. 3. Calibration curve for electroscope.

pared with one in which the frequency in the primary circuit had been lowered, all other factors in both circuits being left undisturbed. As the wave-meter showed practically no change in wave-length, thus indicating impulse excitation, the author concludes that whatever change took place in the spectrum was the result of a change in potential alone.

Voltage determination at 60 cycles. Assuming that the ratio of the voltages of the primary coil to that of the secondary coil remains constant for all potentials, an electroscope was constructed and calibrated having a range of from 0 to 15,000 volts Fig. 3. Peak voltages were obtained by multiplying by $\sqrt{2}$. Voltages computed in this way are shown in Table I.

Results

Chlorine. The tube used in making Plates 125 and 128 (Figs. 4 and 5) was one marked Chlorine *B*, an electrodeless quartz tube. The pressure

in this tube was exceedingly low. Few if any of the lines shown in these spectrograms are due to chlorine. In photographs of the 60 cycle frequency, a great many nitrogen bands appear between λ2800 and λ4100. All photographs of the 60 cycle show similar results, the only difference being that increasing the potential seems to intensity the spectrum. When frequencies of 1.5×10^6 and 1.1×10^6 cycles per second were impressed upon the tube the appearance of the spectrum was almost completely changed. All the nitrogen bands were more or less suppressed and the so-called cyanogen band at λ3884 came out with maximum intensity, extending almost to λ3700. This would seem to throw some doubt upon the opinion held by some,[7,8] that this band is due to the N_2 molecule. It at least suggests a different carrier from that of the other nitrogen bands. The silicon lines at λ2881.7 and 2479.8 were brought out strongly in the high frequency spectra but did not show at all in the 60 cycle spectra. Since the potential over the tube for the 60 cycle frequency was equal to or greater than that of the high frequency spectra, the author believes that these lines were brought out as a direct result of the more rapid vibrations of the high frequency waves.

Helium. Photographs were made from six different helium tubes and from one hydrogen-helium tube. All of these tubes except one, a quartz tube, were obtained from the Hilton-Davis Company and were new tubes. The pressures in these different glass tubes at the time when they were sealed varied between 1 mm and 6 mm. The tube used in making Plate 129 (Fig. 6) had a pressure of 1 mm. A number of lines due to mercury and other impurities appear (See Table I, Plate 129, Fig. 6). The main differences in spectra seem to be that the mercury lines λ5460, 4358 and 4046 of the sharp series, as well as the diffuse triplet λ3663, 3655 and 3650, are greatly intensified by high frequency waves. The quartz tube used in making Plate 132 (Fig. 7) had a very low pressure. Most of the lines and bands shown in the photograph are due to nitrogen. Voltages and frequencies are given in Table I. In the spectrogram of the 60 cycle frequency many nitrogen bands appear, which become less intense as high frequency excitation is impressed upon the tube. At the same time the cyanogen band 3884 comes out brilliantly and lines due to the walls of the tube appear in the ultra-violet. Plate 116 (Fig. 8) shows these changes in a remarkable way. All tubes filled with pure helium at pressures between 1 mm and 6 mm showed no changes in spectra when the frequency was changed from 60 to 1,000,000 alternations per second.

[7] Runge and Grotrian, Phys. Zeits. **15**, 545 (1914).

[8] Sommerfeld, Atomic Structure and Spectral Lines, p. 429; Campbell, Series Spectra, Camb. Phys. Ser., Chap. XV, p. 105.

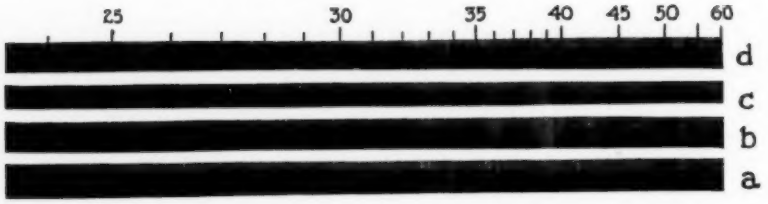

Fig. 4. Plate 125. Chlorine B. Electrodeless quartz tube. Explanation given in Table I.

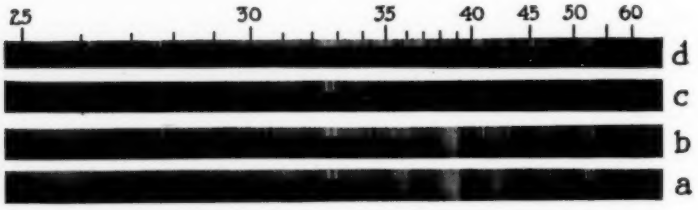

Fig. 5. Plate 128. Chlorine B. Electrodeless quartz tube. Explanation given in Table I.

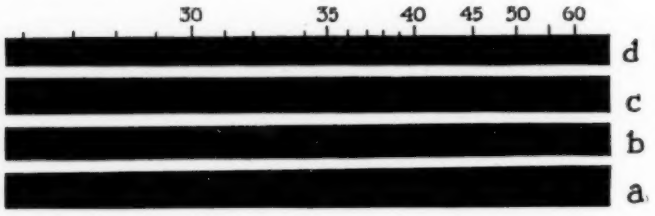

Fig. 6. Plate 129. Helium. Electrodeless glass tube. Explanation given in Table I.

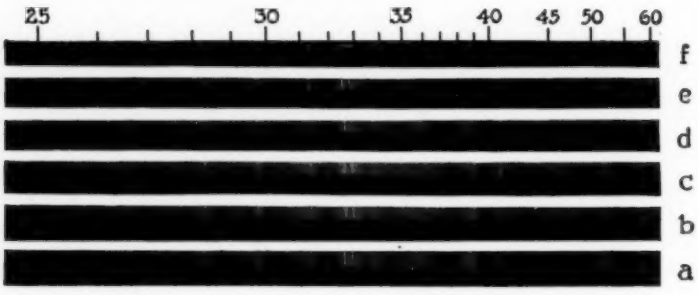

Fig. 7. Plate 132. Helium. Electrodeless quartz tube. Explanation given in Table I.

TABLE I

Conditions under which the spectrograms of Figs. 4, 5, 6, 7 were taken.

Position on scale	Exposure on tube in seconds	Current through secondary of transformer in amperes	Frequency	Capacity in OT primary circuit in microfarads $\times 10^{-6}$	Decrement of wavemeter	Decrement of sending circuit	Scale of electroscope	Potential over tube in volts
			Plate 125 Quartz electrodeless, Chlorine B					
a	30, 20, 10	Small	60	...	.....	.....	....	.....
b	15, 10, 5	0.67	1.11×10^6	350	0.266	0.072	....	14180
c	15, 10, 5	0.73	1.50×10^6	350	0.181	0.091	....	14950
d	60, 40, 20	Small	60	...	.....	.....	....	.....
			Plate 128 Quartz electrodeless, Chlorine B					
a	15, 10, 5	0.71	0.93×10^6	350	0.0594	0.654	....	15630
b	15, 10, 5	0.72	1.48×10^6	350	0.0660	0.460	....	10500
c	60, 40, 20	Small	60	...	.....	.....	61.4	12870
d	30, 20, 10	Small	60	...	.....	.....	73.5	17270
			Plate 129 Helium glass, electrodeless					
a	10, 5, 5	0.30	1.45×10^6	350	0.0475	0.1465	....	7900
b	10, 5, 5	0.30	1.03×10^6	350	0.0667	0.1273	....	8760
c	20, 10, 10	Small	60	...	.....	.....	44.7	8760
d	10, 5, 5	Small	60	...	.....	.....	67.0	14500
			Plate 132 Helium quartz, electrodeless					
a	15, 10, 5	0.78	1.17×10^6	570	0.0588	0.0624	....	9160
b	15, 10, 5	1.21	0.91×10^6	927	0.0762	0.0524	....	9080
c	15, 10, 5	0.80	0.58×10^6	681	0.0842	0.0427	....	9260
d	15, 10, 5	0.77	1.91×10^6	500	0.0360	0.0780	....	9270
e	60, 40, 20	Small	60	...	.....	.....	46.1	9190
f	30, 20, 10	Small	60	...	.....	.....	74.0	17600

Neon. A quartz electrodeless tube gave spectrograms showing no changes in spectra for slight changes in frequency, i.e., from 0.4×10^6 to 1.5×10^6 alternations per second. Marked differences were shown, however, when compared to the 60 cycle spectrum. A great many lines appeared in the violet and ultra-violet end of the high frequency spectrum which either did not appear at all in the 60 cycle spectrum, or appeared with reduced intensities. Two new neon tubes, which had not been used previously and which had pressures of approximately 6 mm at the time they were sealed, indicated no changes in spectra when the frequency was changed from 60 to 1,000,000 alternations per second.

Krypton. It was noticed in the case of an electrodeless quartz tube, that, if resonance conditions were established in the oscillating circuits

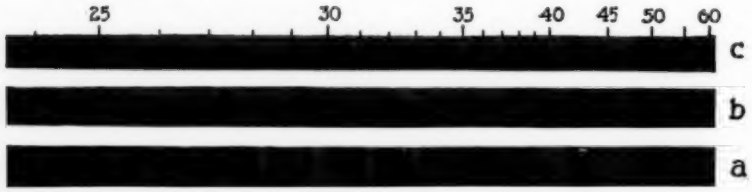

Fig. 8. Plate 116. Helium. Electrodeless quartz tube. (a) Freq. 60; exp. 10-20-30 min.; current less than 1 m.a. (b) Freq., resonance, 1.48×10^6; exp. 10-20-30 min.; current through tube 40 m.a. (c) Freq. in secondary, 1.48×10^6, in primary 0.91×10^6; exp. 10-20-30 min.; current through tube 15 m.a.

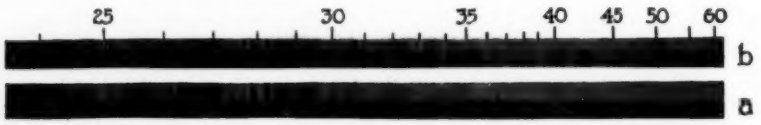

Fig. 9. Plate 109. Krypton. Electrodeless quartz tube. (a) Freq. in secondary, 1.70×10^6, in primary 0.84×10^6; exp. 40-20 min.; current through tube 25 m.a. (b) Freq., 1.70×10^6, resonance; exp. 16-14 min.; current through tube 75 m.a.

and the inductance of the tuning coil in the primary circuit changed gradually the color of the light given out changed from a bright blue to a pale yellow. The differences in spectra are shown in Plate 109 (Fig. 9). A number of plates were exposed each time with the same results. Upon closer inspection it was found, that, when conditions were such as to produce the yellow light, only two main lines appeared in the visible spectrum, the yellow line and the green line. In addition to these there were a few blue and violet lines, which appeared with greater intensity on the photographic plate than to the naked eye. As the inductance in the primary circuit was brought nearer its resonance value, line after line appeared in the violet and ultra-violet, while the yellow line and

green line, mentioned above, became somewhat weaker in intensity. At the same time the point of maximum energy was shifted toward the violet. As the wave-meter indicated that practically no change in frequency had occurred, the difference was attributed to a change in potential. At resonance the potential as indicated by the sparking distance was approximately four times as high.

Hydrogen, mercury and xenon. A few spectrograms were made from hydrogen and xenon tubes, but no changes worth mentioning were found. One mercury plate showed marked differences between the 60 cycle spectra and the high frequency spectra; but, as the tube had to be heated in order to get the discharge through it, little significance was attributed to these changes. It is known[2] that the spectrum of a heated mercury tube is quite different after heating from what it was before heating.

Conclusions

The results obtained from these experiments seem to warrant the following conclusions:

1. That the spectra of the gases, hydrogen, helium, neon, krypton, xenon, nitrogen, mercury and chlorine, in no case show differences in spectra for changes in frequency between 2×10^6 and 0.4×10^6 alternations per second, when the potential is kept approximately constant.

2. That the high frequency spectra and 60 cycle spectra of the gases studied appear to be identical for pressures between 1 mm and 6 mm.

3. That for low pressures high frequency spectra differ widely from the 60 cycle spectra in neon, krypton and in chlorine or helium tubes containing nitrogen.

4. That mercury when existing as an impurity in a helium tube comes out more strongly when stimulated with Tesla frequencies than when stimulated with 60 cycle frequencies of equal potential. Especially is this true of the lines λ5460, 4358 and 4046 of the sharp series and the diffuse triplet λ3662.8, 3654.8 and 3650.1. Slight changes in frequency, however, seem to produce no differences in spectra.

5. That in chlorine tubes containing nitrogen, the nitrogen bands are brought out much more intensely by the 60 cycle currents than by high frequency currents with possibly one exception. The so-called cyanogen band at λ3884 is greatly intensified by high frequency currents. This would seem to throw some doubt on its being due to the N_2 molecule as suggested by Runge and Grotrian.[7]

6. That lines due to the walls of the tube are at the same voltage more easily brought out in high frequency spectra than in 60 cycle spectra. Especially is this true of the silicon lines λ2881.7 and 2479.8. These lines appear in the spectra of both quartz and glass tubes.

7. That the characteristic differences between 60 cycle spectra and high frequency spectra are not due to a change in potential but rather to some sort of a trigger action on the part of the high frequency waves which make possible the release in the atom of a greater variety of quanta.

In conclusion the author wishes to express his thanks to Dr. A. L. Foley of Indiana University, who suggested the problem and under whose direction the work was done. Thanks are likewise due Dr. R. R. Ramsey for many helpful suggestions on the electrical side of the problem, and to John G. Moorhead, with whom the author was associated in the earlier part of this work.

WESTMINSTER COLLEGE,
NEW WILMINGTON, PA.
July 24, 1926.

THE TIME INTERVALS BETWEEN THE APPEARANCE OF CERTAIN SPECTRUM LINES OF HELIUM AND OF MERCURY

By J. W. Beams* and P. N. Rhodes

Abstract

The times between the appearance of certain lines in the visible region of the spectrum of helium and of mercury have been measured by a method previously described. The results are tabulated. The time intervals were found to be independent of the conditions of excitation of the spectrum lines and are believed to be of the same order of magnitude as the differences in the total times between excitation and emission of the various lines investigated.

A METHOD for the study of the time of appearance of spectrum lines in the beginning of spark and condensed discharges has been recently developed.[1,2] It was found that the times between the appearance of the spectrum lines of the elements investigated are practically independent of the conditions of excitation,[3] and are of the same order of magnitude as the differences in the total time from excitation to emission for various spectrum lines which would be expected from the experiments of McPetrie[4] and others,[5] on the average time an atom remains in the excited state before emission. The above work has been extended and this paper gives the results for the visible region of the spectra of helium and mercury.

The experimental method is the same as that previously described in detail.[2] In the case of helium most of the observations were taken with the gas at 6 to 8 mm pressure in a very short discharge tube of the H type so constructed as to permit the capillary to be viewed end-on through ring electrodes co-axial with it. The spectrum of a spark through helium at atmospheric pressure was also studied, but under these conditions most of the parhelium lines were too faint to permit of accurate time interval measurements. However, good readings were obtained with orthohelium lines and the results agree within experimental error with those taken by means of the discharge tube.

In the case of mercury, a discharge tube similar in type to the helium tube, and containing a few globules of mercury, was strongly heated

* National Research Fellow.

[1] Brown and Beams, J.O.S.A. **11**, 11 (1925).

[2] Beams, Phys. Rev. **28**, 475 (1926).

[3] Beams, Phys. Rev. **27**, 805A (1926).

[4] McPetrie Phil. Mag. **1**, 1082 (1926).

[5] See Foote and Mohler, Origin of Spectra, p. 93.

with a bunsen flame in a porcelain container, so constructed that an unobstructed end-on view of the capillary could be obtained. Under the influence of heat and a heavy discharge a rich spectrum was obtained in which a few of the spark lines were of an intensity almost equal to that of the arc lines. The fact that the tube had to be strongly heated gave opportunity for observations under different conditions of temperature, and therefore, of different vapor pressures of mercury. The intensity of the different spark lines varied considerably, being greatest at the highest temperatures, but no changes in time intervals were noted in the case of either spark or arc lines from the maximum temperature the tube could stand without burning up the electrodes, down to a temperature so low that a discharge would not take place in the tube. Furthermore, in the cases of several lines, observations were taken using a mercury spark in air in place of the discharge tube with no observed

TABLE I

Time intervals between the appearance of certain spectrum lines of helium and mercury.

Wave-length in Ångstrom units	Type of line	Integrated intensity Helium	Revised Paschen series notation	Time intervals in sec$\times 10^8$
4686	Spark	4	First member Fowler series	(not measured)
5016	Parhelium	6	$2S-3P$	1.20
4922	Parhelium	5	$2P-4D$	.07
4472	Orthohelium	10	$2p_{1,2}-4D$	2.47
5876	Orthohelium	10	$2p_{1,2}-3d$	2.27
4713	Orthohelium	4	$2p_{1,2}-3s$	5.06
6678	Parhelium	6	$2P-3D$	(doubtful)
		Mercury		
5427*	Spark	8		2.55
5679*	Spark	6		.30
5872*	Spark	4		.46
5461	Arc	10	$2p_1-2s$	1.13
4340 **	Arc	10	$2P-4d_2$	
4344			$2P-4d_3$	
4348			$2P-4D$	
4358			$2p_2-2s$	1.73
5770 **	Arc	10	$2P-3d_2$	
5790			$2P-3d_3$	
5791			$2P-3D$	2.89
6235	Arc	5	$2S-5P$	(very doubtful)

*Notation not established.
**Unresolved.

differences greater than experimental error. Table I gives the results obtained. The precision of the measurements was at least $.3\times10^{-8}$ sec.

It will be noted that in the cases of both helium and mercury the spark lines appear first. This is in accord with the results previously found with cadmium, magnesium, zinc and nitrogen,[2] and lends support to the idea that if the degree of ionization is increased the probability of an electron jump is likewise increased, and thus the time between the excitation and the emission of a spectrum line is decreased. This might be expected because of the higher electric field in the neighborhood of multiply ionized atoms as compared with atoms only excited. This, however, does not hold unless there is a large difference in the electric fields because the time of appearance of lines emitted by an atom while in the same stage of ionization is certainly not a simple function of the energy values assigned to the various upper levels or to the frequency of the line emitted.

In the case of helium, the parhelium lines $2S-3P$ and $2P-4D$ appear before the bright orthohelium lines, but the parhelium line $2P-3D$ is the last to appear. This latter observation is interesting because the lines $2P-4D$ and $2P-3D$ belong to the same series, yet are observed to appear almost 10^{-7} seconds apart. As is indicated in the table, the time of appearance of $2P-3D$ is doubtful, since the sensitivity of both the eye and of the photographic plate decreases in this region, yet the value given is probably of the right order of magnitude.

In the orthohelium spectrum the observed lines have the same $p_{1,2}$ final levels but different initial levels. The results then indicate that the electron remains on the average about 2.47×10^{-8} sec. longer in the $3d$ energy level than in the $4d$ energy level, and 2.27×10^{-8} sec. longer in the $3s$ energy level than in the $3d$ level. It is unfortunate that these close orthohelium doublets could not be resolved, for if a time existed between the appearance of the two members of the doublet, then this time should be a function of the $p_{1,2}$ levels only, and hence practically the same for each of the doublets.

In considering mercury no conclusions can as yet be drawn from the sequence of the spark lines as their spectroscopic notation has not been established. In the arc spectrum the line $2p_1-2s$ appears before $2p_2-2s$, which is in accord with the results found previously for cadmium, zinc, and nitrogen, and strengthens the emphasis placed there upon the importance of the final level in determining the time before emission. It is to be regretted that under the conditions of observation the members of the two groups which have the same $2P$ level could not be clearly separated, but it is hoped that this will be overcome in future work.

In conclusion the authors wish to acknowledge their indebtedness to Professors L. G. Hoxton, C. M. Sparrow, and F. L. Brown for many helpful suggestions, and to Mr. A. J. Weed, instrument maker, for aid in the construction of apparatus. A supply of helium for part of the work was made available through the courtesy of Mr. Scott Turner, Director of the Bureau of Mines.

ROUSS PHYSICAL LABORATORY,
UNIVERSITY OF VIRGINIA,
July 20, 1926.

POLARIZATION BY ELECTRON IMPACT

By J. A. Eldridge and H. F. Olson

Abstract

If the spectrum excited by low velocity electrons in mercury vapor at low pressure be observed from a direction normal to the electron beam it has been found that many of the lines are polarized (Ellett, Foote and Mohler, and Skinner). Except when the excited atom is in a state having a minimum value for j, the usual theory predicts such polarization, and further indicates that the polarization (electric vector) should be parallel to the electron stream for lines which have $\Delta j = \pm 1$ and normal to the electron stream when $\Delta j = 0$. The observation shows that for the first subordinate series the polarization is in accord with this theory. For the second subordinate series the polarization is always much weaker, and the indication is that the sense of this polarization is not in agreement with that predicted by theory.

ELLETT, Foote and Mohler[1] have pointed out that when an electron having the energy required to cause an electronic displacement collides with an atom that the change in angular momentum of the atom (proportional to Δj) must have its vectorial direction in a plane normal to the velocity of the electron. This is quite easily seen. The angular momentum of this impacting electron with respect to any nearby atomic center is in a plane normal to the velocity. Since after collision its velocity is zero, the *change* in the angular momentum is perpendicular to the velocity. So it is for the exciting electron and so it must be for the excited atom.

If the energy is greater than this critical value so that after collision some velocity is retained the angular momentum given to the atom will no longer be confined to this normal plane but may be in directions making considerably less than 90° with the velocity the electron had before striking. Indeed we may suppose that the direction of Δj will be the more nearly in this plane the smaller v and the larger Δj. If Δj is 0 there is no reason to expect selective orientation.

The actual direction of the angular momentum of the atom in space will be given by the vector sum $j_s + \Delta j$ where j_s is the angular momentum of the initial ($1S$) state. j_s is 0, $\frac{1}{2}$ or 1 according respectively to Sommerfeld, Landé and Bohr. Consequently, unless we adopt Sommerfeld's hypothesis, the actual direction of j will depart somewhat from the direction of Δj and particularly will this be the case for small values of j.

[1] Ellett, Foote and Mohler, Phys. Rev. **27**, 31 (1926).

Take the specific case mercury vapor. If the vapor be excited by an electron stream having a velocity higher than the ionizing velocity, the electrons will be displaced from the normal $1S$ orbit to higher orbits and usually to orbits with greater angular momenta and the j vectors will in this excited state be, to some degree of approximation, confined to the normal plane. Exceptions are the nS and np_3 orbits which have the same inner quantum numbers ($\frac{1}{2}$ according to Landé) as the $1S$ orbit. It is probable that this orientation will be more exactly obtained for the $d_1(j=7/2)$, the d_2, D, $p_1(j=5/2)$ orbits than for the d_3, p_2, P and $s(j=3/2)$ orbits.

Granting this approximate orientation it is possible from the correspondence principle to predict the type of polarization. It follows from this principle if $\Delta j=\pm 1$ that the light given out by the atom should be circularly polarized about Δj axis and if $\Delta j=0$ the light is linearly polarized along the j axis (the Δj refers at present to the change occurring in the return of the electron and is not to be confused with the Δj of the former paragraph). We may suppose for simplicity that the Δj of the returning electron is a vector in the same direction as j itself.

If the beam of electrons be sent in the direction v and the tube be viewed perpendicularly to the beam as shown in Fig. 1 the atoms in all

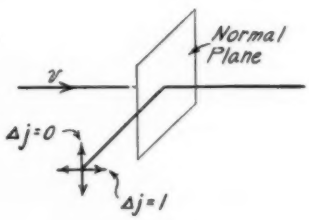

Fig. 1.

states other than nS and np_1 will be oriented according to this theory approximately in the plane normal to v. Transitions from such a state involving $\Delta j=0$ should result in lines polarized perpendicularly to the electron stream. Transitions involving $\Delta j=\pm 1$ which give out light circularly polarized at random directions in the normal plane result, in statistical aggregate, in light polarized parallel to the electron stream. The maximum possible value for perfect atomic orientations will be 100 percent for the perpendicular lines and 33 percent for the paraliel.

Ellett, Foote and Mohler excited the line $1S-2p_2$ ($\lambda 2537$) with voltages slightly above the resonance potential and found this line perpendicularly polarized, contrary to theory. Because of the long life of the $2p_2$ state, this polarization is found only at very low pressures

and with a neutralized earth's field. Skinner,[2] examining the visible mercury spectrum, found the lines originating in s or S orbits unpolarized. Those originating in d or D orbits (with one exception) were polarized in every case parallel to the current.

The present writers have observed the polarization of the lines of the mercury spectrum from λ2400 to λ4400 with greater dispersion than used by Skinner, who was unable to resolve the d, D levels. The tube used is shown diagrammatically in Fig. 2. A Pyrex tube was lined with a

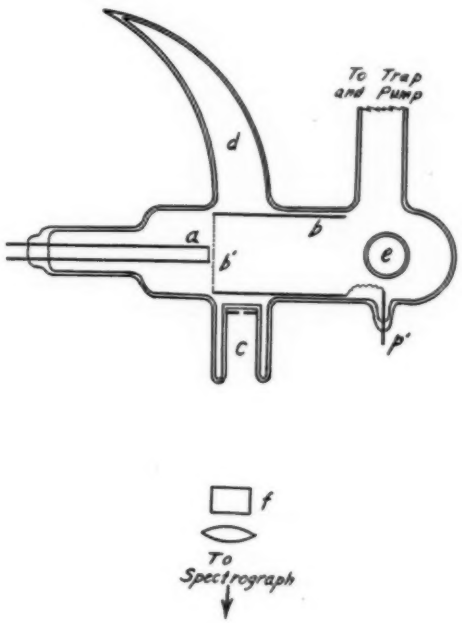

Fig. 2. Diagram of apparatus.

copper cylinder b and gauze b'. An oxide coated platinum strip a electrically heated placed within 1 or 2 mm of the gauze served as a cathode giving a well defined stream of electrons when suitable voltage was applied to b'. A well e containing mercury could be maintained at any desired temperature. At c a reentrant quartz window was sealed to a table containing a suitable diaphragm and opposite it was a light trap d. The light through the diaphragm opening was focussed on the slit of a quartz spectrograph being first separated into two oppositely polarized images by means of a Wollaston prism f. A large quartz spectrograph, Hilger, 2 meter focus, Littrow mount, was used.

[2] Skinner, Nature **117**, 418 (1926).

For the lines investigated (which did not include λ2537) the amount of polarization is not greatly affected by the vapor pressure even when the mercury is kept at a temperature as high as 60°C. Only when conditions are such that an arc is started in the tube, is the polarization greatly reduced. The results here presented were obtained at room temperature. Since, as one would expect, the polarization is weakened at higher voltages, it was found advisable to work within two volts of the ionization potential. Under the conditions of the experiment the emission is not very strong and exposures of several days were necessary to bring out some of the weaker lines. The results are given in Table I.

TABLE I

λ	Transition	Pol	Δ_j	λ	Transition	Pol	Δ_j
4358	$2p_2-2s$	∥	0	3021	$2p_1-4d_1$	∥	−1
4344	$2P-4D$	∥	−1	2967	$2p_3-3d_3$	Weak ⊥	−1
4108	$2P-4S$	Weak	+1	2925	$2p_1-4s$	Weak	+1
4077	$2p_2-2S$	Weak	+1	2894	$2p_2-3s$	∥	0
4047	$2p_2-2s$	Weak	−1	2848	$2p_2-3S$	∥	+1
3907	$2P-5D$	∥	−1	2804	$2p_1-5d_2$	⊥	0
3663	$2p_1-3D$	⊥	0	2803	$2p_1-5d_1$	∥	−1
3655	$2p_1-3d_2$	⊥	0	2760	$2p_1-5s$	Weak	+1
3650	$2p_1-3d_1$	∥	−1	2753	$2p_2-3s$	Weak	−1
3341	$2p_1-3s$	Weak	+1	2701	$2p_1-5D$	⊥	0
3131	$2p_2-3D$	∥	−1	2700	$2p_1-5d_2$	⊥	0
3125	$2p_2-3d_2$	∥	−1	2699	$2p_1-5d_1$	∥	−1
3027	$2p_1-4D$	⊥	0	2655	$2p_2-4D$	∥	−1
3026	$2p_1-4d_3$	Weak	+1	2653	$2p_2-4d_3$	Weak	0
3023	$2p_1-4d_2$	⊥	0	2652	$2p_2-4d_2$	∥	−1

We have been unable to measure with consistency the polarization of the more weakly polarized lines. Our results agree with those of Skinner to the extent that we find that lines corresponding to transitions from the *s* or *S* orbits are polarized weakly if at all. There seemed to be no question as to the polarization in some cases but for the most part, though it is very likely that some small amount of polarization is present, it is not great for these lines and we have not indicated the trace of polarization found in these cases.

According to the theory no polarization is expected in the case of the terms involving *S* since there is in the theory no reason to expect atomic orientation; no change of angular momentum takes place at the impact. The observation shows that the polarization for these lines is usually certainly very small. The polarization of terms involving *s* is equally weak and this is less easily accounted for. The value of *j* in this case is not large and from the theory sketched above we might expect the atomic orientation to be much less perfect in such a case than when a level having a large angular momentum is involved. The difficulty

is that in some cases these lines are definitely polarized and in other cases probably polarized slightly and in such cases the polarization is as often as not contrary to the theory. The first line in the table illustrates this point.

Considering, now, lines corresponding to transitions from the $d(D)$ levels, lines of the first subordinate series, one finds in most cases very striking polarization, the one component being often two or three times as strong as the oppositely polarized component. In these cases, which usually involve large values of j, we expect the orientation of the atom to be most perfect and for these lines there is close agreement between our results and those predicted from the theory. Indeed this agreement is perfect except that in the case of transitions from the d_3 level the polarization is weak and our results have not been entirely consistent. The line $2p_3-3d_3$ should be polarized parallel and this line is unquestionably so polarized, though the polarization is not strong. The lines $2p_1-3d_3$ and $2p_2-3d_3$ cannot be observed as they were not separated from the stronger lines $2p_1-3D$ and $2p_2-3D$. The higher members $2p_1-4d_3$ and $2p_2-4d_3$ are polarized weakly and our observations have not been consistent for these lines. This is not very satisfactory, yet it does appear to be in line with our other observations. It should be noticed that the value of j in this case is only 3/2 (Landé) and from the results in the case of the s terms we are led to believe that small values of j are accompanied by weak polarizations and polarizations as often as not contrary to theory.

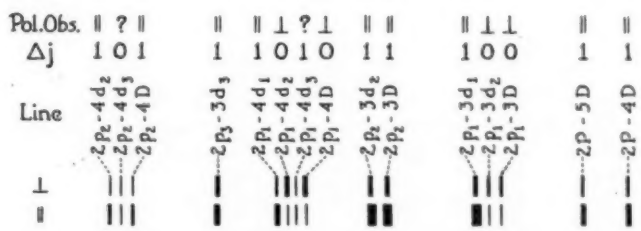

Fig. 3. Graphical representation of results for the first subordinate series of mercury

In Fig. 3 are presented graphically the results in the case of the first subordinate series. We show here the two oppositely polarized spectra, somewhat as they appear in the spectrographs except that the components of the triplet have been separated for the sake of clearness.

It appears that for larger values of j there is a good agreement between our results and the theory. The agreement with the theory for the larger values of angular momentum and disagreement for the smaller

reminds one somewhat of the correspondence which so often occurs between atomic phenomena and classical theory for the larger orbits. Whether there is indeed much significance in the generalization which we have made can only be determined by an extension of the work.

HALL OF PHYSICS,
UNIVERSITY OF IOWA,
September 24, 1926.

Note (November 1, 1926). In a recent paper Skinner gives results which are in substantial agreement with those presented in this paper. (Proc. Roy. Soc., October, 1926.) In this paper we have used the concept of Rubinowicz that the atom emits circularly or linearly polarized light according as its angular momentum does or does not change. Skinner invokes the hypothesis of spectroscopic stability to account for the sign polarization. Either theory suffices to explain qualitatively the results in the diffuse subordinate series and neither explains satisfactorily results in other series. However it appears from recent quantitative measurement that in at least one case ($2P$—$4D$) it is possible to obtain a line polarized 60% parallel to the exciting current. The theory as developed above permits but 33% polarization parallel to the current. Indeed such a result seems quite inexplicable by a theory (such as that of Rubinowicz) which assumes the radiation in question is composed of circularly polarized light quanta; such a result supports the hypothesis of spectroscopic stability. To be sure by substituting the concept of elliptically polarized for circularly polarized light the theory given above could probably be made to accomodate this quantitative result.

THE BAND SPECTRA OF CARBON MONOXIDE

By Raymond T. Birge

Abstract

All of the numerous band spectra formerly attributed to carbon are due probably to carbon compounds. A majority of those analyzed are now definitely known to be due to carbon monoxide, as a result of the intercorrelation of the various systems and the correlation of one of these systems, the fourth positive group of carbon, with the known absorption spectrum of CO.

The known band spectra of neutral carbon monoxide comprise the fourth positive group of carbon, the Ångström CO bands, the Cameron bands, and the third positive group of carbon,—this latter group having been shown by Duffendack and Fox to comprise in reality two different systems. The relation of these various systems is indicated in Fig. 1 and Table I. The band systems of ionized carbon monoxide,—i.e., the comet-tail bands, the first negative group of carbon, and the Baldet-Johnson combination bands,—are also shown in this figure.

The fourth positive group of carbon, as analyzed by the writer, comprises the former group of that name, and also Lyman's fifth positive group, and practically all the remaining unassigned bands found by Lyman in the ultra-violet spectrum of carbon monoxide. Full details of this analysis are given, and the results are tabulated in Table II and in Fig. 2. The bands found by Leifson in the absorption spectrum of cold carbon monoxide form a selected portion of this system, proving that it is the "resonance" system of CO. The system is also quantitatively related to the known infra-red absorption bands of CO in the manner demanded by the quantum theory. The general intensity distribution is in agreement with Franck's mechanical theory, as extended by Condon. The vibrational data obtained from this system have been used by Birge and Sponer to calculate the heat of dissociation of CO.

The Ångström CO bands have as a final state the initial state of the fourth group, and this relation permits a definite assignment of vibrational quantum numbers for the Ångström bands. Recent work by Jassé on the fine structure of these bands is in agreement with this assignment. All of the measurements on the heads of the Ångström bands are collected in Table III and are compared with the calculated values. A puzzling discrepancy in one of the vibrational energy intervals is noted and discussed.

The Cameron bands and the third positive group of carbon have been found by Johnson to have the same relation as the above two systems, and the Cameron bands form a second "resonance" system for CO. They have recently been found in absorption, by Hopfield. The common electronic level of these two systems is probably triple, although the bands of each system have either five-fold or six-fold heads. The various relations are discussed in detail, and equations are given in all cases.

Recent work indicates that the electronic energy levels of molecules are similar to those found in atoms, and an assumed octet structure for CO suggests its correlation with Mg. The actual details of this correlation are given, but no attempt is made to discuss critically the underlying theory. The levels for CO are shown to be either single or triple, and the only two levels belonging to the same term sequence are found to fit a Rydberg formula with the known correct limit.

Introduction

ON PAGES 226–234 of Vol. V of Kayser's "Handbuch der Spectroscopie," and on pages 131–147 of Vol. VII, part 1, there are listed the various band spectra assumed due to carbon or its compounds. It would appear at the present time that none of these spectra are due to the molecule of carbon, and it is doubtful if such a molecule (diatomic) exists. The violet and red cyanogen bands are almost certainly due to the molecule CN,[1] and the so-called C+H bands to the molecule CH.[2] The Swan bands are probably due to C_2H_2, but this is still very uncertain.[3] The group of Deslandres and d'Azambuja,[4] and the second negative group of Deslandres and d'Azambuja[4] are so incompletely known that it is not possible as yet to give even an empirical analysis. The high pressure CO bands of Fowler[5] and the triplet bands of Merton and Johnson[6] can be analyzed and reasonably certain quantum assignments made.[7] The chemical origin of these four systems is however not known with certainty. All of the remaining band systems listed under *carbon* in the Handbuch, as well as others discovered quite recently, are definitely known to be due to CO or CO^+, and form the subject of this paper.

Until very recently it was impossible to give the exact chemical origin of practically any band system, even of those most exhaustively investigated. The long controversy concerning the Swan bands[3,8] is a case in point. The striking advance made within the past year or two rests mainly upon the discovery of two related facts, (1) the identity of numerical constants in certain different band systems, proving that all the systems thus related must be due to the same chemical molecule, (2) the discovery of at least *one* of these related systems in absorption in the cold (or fairly cool) vapor of some known molecule. A further criterion, which in many cases is sufficient for the identification, is the evaluation of the moment of inertia of the molecule. This last is the deciding factor in assigning the C+H bands to CH, and the Swan bands to some sym-

[1] Birge, Phys. Rev. **23**, 294 (1924); Mulliken, Nature **114**, 858 (1924); Freundlich and Hochheim, Zeits. f. Physik **26**, 102 (1924); Holst and Oosterhuis, K. Akad. Amster. Proc. **23**, 727 (1921); and Kayser VII, pp. 131–135.

[2] Kratzer, Zeits. f. Physik. **23**, 298 (1924), and Chap. IV, Sections 7 and 8, Report of the National Research Council on "Molecular Spectra in Gases" (in press). This last reference will be referred to as "Report."

[3] Shea and Birge, Phys. Rev. **27**, 245 (1926), and Johnson, Nature **116**, 539, Oct. 10 (1925).

[4] Deslandres and d'Azambuja, Compt. rendus **140**, 917 (1905).

[5] A. Fowler, M. N. Roy. Ast. Soc. **70**, 484 (1910).

[6] Merton and Johnson, Proc. Roy. Soc. **103A**, 383 (1923).

[7] Birge, Nature **116**, 170, Aug. 1 (1925).

[8] Watts, Phil. Mag. (6) **28**, 117 (1914), and Kayser VII, pp. 139–141.

metrical molecule of approximately the mass of acetylene. In certain cases the measured isotopic effect has made it possible to discriminate between two molecules as possible emitters of the bands. Still further methods of identification have been used, but they are less direct than those just mentioned.

In the present paper we are concerned primarily with the relations between the various bands forming a system, evaluating the vibrational energy levels of the system, and between the various systems, evaluating the electronic energy levels of the molecule. A rather detailed account of the quantum theory of band spectra is given in the Report of the National Research Council on "Molecular Spectra in Gases" (in press), and no attempt at repetition will be made here.

The Spectra of Neutral Carbon Monoxide

The first step in the establishment of the system of energy levels of CO was made by the writer,[9] as a result of the quantum analysis of the extensive set of bands in the ultra-violet, usually attributed to CO.[10] A small portion of this system had been called by Deslandres[11] the "fourth positive group of carbon," and a small part of the remaining bands had been called by Lyman[12] the "fifth positive group of carbon." On completion of the analysis, the writer found that the $n''=0$ progression of this new system appeared on Leifson's[13] absorption spectrum of CO. This definitely established the lower (n'') level as the normal level of the CO molecule. At the same time it was found that the upper (n') level of the new system was also the lower level of the Ångström CO bands, thereby proving that these latter bands were due to neutral CO, as commonly assumed, and also evaluating three electronic energy levels of CO. This work has been briefly reported,[9] and the theoretical interpretation of the results has been given in another short article.[14]

Later, R. C. Johnson[15] found it possible to obtain a similar correlation of the third positive group of carbon with the newly discovered Cameron bands.[16] By using the writer's results for the fourth positive group, Johnson was able to show that the Cameron bands had the same final level. Hence these two additional systems are due to CO, and the band

[9] Birge, Nature **117**, 229, Feb. 13 (1926).

[10] Lyman, Spectroscopy of the Extreme Ultra-violet, pp. 84 and 114.

[11] Deslandres, Compt. rendus. **106**, 842 (1888), and Ann. chim. et phys. (6) **15**, 5 (1888). The second reference contains a drawing of the system.

[12] Lyman, Proc. Amer. Acad. Arts **45**, 315 (1909).

[13] Leifson, Astrophys. J. **63**, 73 (1926).

[14] Birge, Nature **117**, 300, Feb. 27 (1926).

[15] Johnson, Nature **117**, 376, Mar. 13 (1926).

[16] Cameron, Phil. Mag. **1**, 405 (1926).

spectra evaluate two more electronic levels. The theoretical interpretation of the new levels was made immediately by Dr. R. S. Mulliken and by the writer, and is given by Johnson.[17] Recently Duffendack and

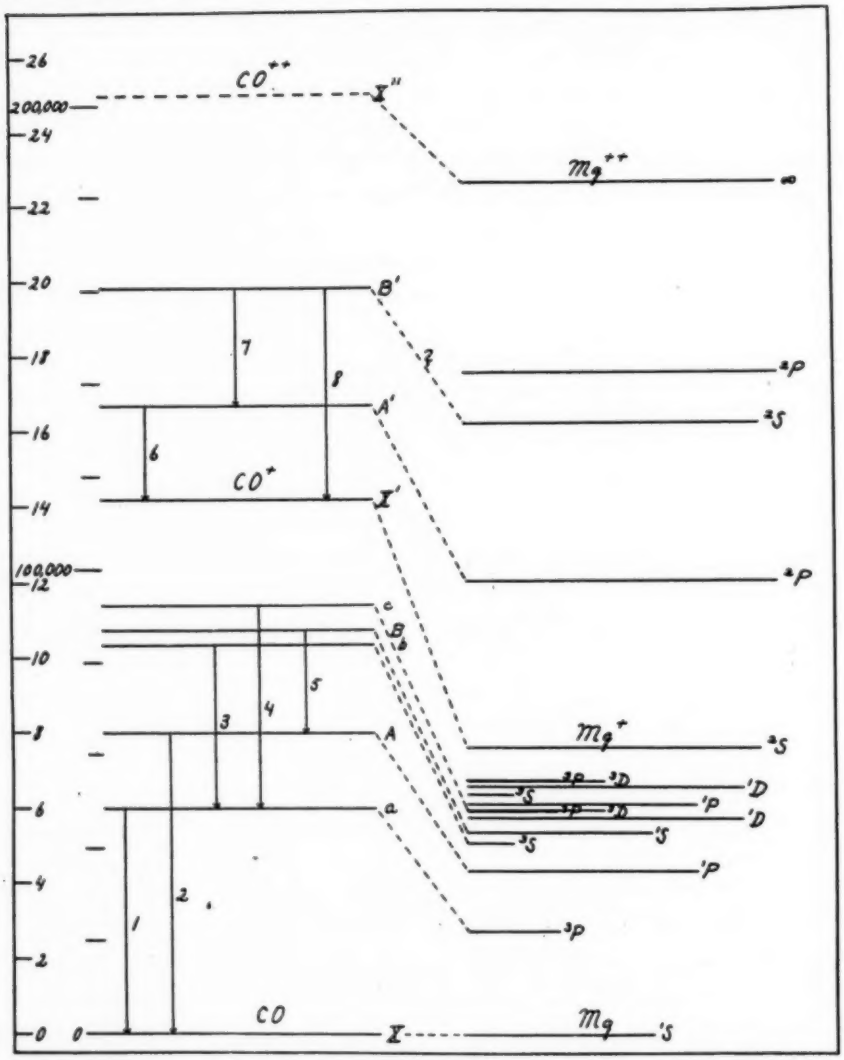

Fig. 1. Electronic energy levels for CO, CO^+, Mg and Mg^+. 1, Cameron CO bands; 2, fourth positive group of carbon; 3, third positive group of carbon; 4, 3A bands of third positive group; 5, Ångström bands of CO; 6, comet-tail bands; 7, combination bands of Baldet-Johnson; 8, first negative group of carbon.

Fox[18] have found that the third positive group is really the superposition of two systems, and the new system, called the 3A bands, has the same

[17] Johnson, Nature **118**, 50, July 10 (1926).
[18] Duffendack and Fox, Nature **118**, 12, July 3 (1926).

final (lower) level as the other, but a different initial level. This initial level thus constitutes a new, sixth, electronic energy level for CO. All of these relations are shown on Fig. 1, which gives also the electronic levels for CO^+.[19] The scale on the left gives both wave numbers (cm^{-1}) and volts, the former running from zero to 200,000, the latter from zero to 26. (One volt = 8100 cm^{-1} approx.) The exact values for the various levels are given in columns 3 and 4 of Table I, and these are discussed in detail later. The separation of any two levels is given by the frequency of the origin of the 0–0 band of the system due to the transition between these two levels. In some cases the fine structure of the bands is not yet known, and the frequency of the head of the 0–0 band is used in the diagram.

TABLE I

Energy levels of carbon monoxide

1	2	3 cm^{-1}	4 volts	5 term	6 D	7 ω''
X	^1S	0	0	114,966	0.9767	2149.7
a	^3P	48,426.3	5.981	66,540	1.2839	1724.8
		to	to	to	to	
		48,529.9	5.994	66,436	1.2849	
A	^1P	64,737	7.995	50,229	1.4777	1497.3
b	^3S	83,817	10.352	31,149	1.8765	(2214)
B	^1S	86,894	10.732	28,072	1.9766	2158
c	?	92,086	11.374	22,880	2.1894	
X'	^2S	114,966	14.200			2197.0
A'	^2P	135,312	16.713			1550.5
		135,438	16.728			
B'	^2S	160,604	19.837			1697.8

THE SPECTRA OF IONIZED CARBON MONOXIDE

Three systems of bands are almost certainly due to CO^+,—the first negative group of carbon, the comet-tail bands, and the Baldet-Johnson "combination" bands. The writer[7] showed definitely that the first two systems had the same final state, and therefore were due to the same molecule, thus confirming the experimental evidence.[20] Blackburn[21] independently reached the same conclusion. Then Mulliken,[22] Mecke,[23] and the writer[24] independently noted that the new bands measured by

[19] A more complete diagram, showing also the vibrational levels, has been published by Birge and Sponer, Phys. Rev. **28**, 259 (1926).

[20] Lemon, Proc. Nat. Acad. Sci. **11**, 41 (1925).

[21] Blackburn, Phys. Rev. **25**, 888 (1925).

[22] Mulliken, Phys. Rev. **26**, 561 (1925).

[23] Mecke, Naturwiss. **13**, 698 (1925).

[24] Birge, Nature **116**, 207, Aug. 8 (1925).

Johnson[25] (a few of which had previously been observed by Baldet[26]) formed a new system having for its initial state the initial state of the first negative group of carbon, and for its final state, the initial state of the comet-tail bands. The importance of such a relation was emphasized by the writer,[24] and it is to be hoped that fine structure measurements of these new bands will soon be available.

The conclusion that all three systems are due to CO^+ is based on the fact that all experimental evidence points to the comet-tail bands as being due to some form of CO,[27] while the first negative group of carbon is, as the name indicates,[28] presumably due to a positive ion. Additional relations found by Birge and Sponer,[19] between the molecular constants of CO and CO^+, assuming the above conclusions, form confirmatory evidence.

We now proceed to a more detailed discussion of the various systems of neutral carbon monoxide, considering in particular the new ultra-violet system which includes the old fourth positive group of carbon, and may conveniently be given that designation. Details regarding the spectra of ionized CO will be given in a separate paper.

The Fourth Positive Group of Carbon

(*a*) Experimental

The fourth positive group of carbon, as measured by Deslandres,[11] consisted of 42 bands, extending from λ2631 to λ2045. The bands are degraded to the red, not to the violet as stated on page 233 of Kayser, Vol. V. Deslandres gives also the relative intensity of the various bands, and Hof[29] later used Deslandres' measurements, but gave another list of intensities for 28 of these bands. Bair,[30] in 1920, measured 22 bands lying between λ2262 and λ1946, but again with small dispersion (probable error several tenths of an Angstrom). Meanwhile Lyman[12] had found, in agreement with Schumann's earlier work, that nearly all vacuum tubes showed a set of bands in the extreme ultra-violet, due evidently to an impurity. The evidence indicated that this was carbon monoxide.

[25] Johnson, Proc. Roy. Soc. **108A**, 343 (1925).

[26] Baldet, Compt. rendus. **178**, 1525 (1924). See also Baldet, Nature **116**, 360, Sept. 5 (1925) and Johnson, Nature **116**, 539, Oct. 10 (1925) as to experimental priority.

[27] See references (5), (6), (26) and (20).

[28] A negative group is one predominantly strong near the negative electrode of the discharge. See Blackburn, Proc. Nat. Acad. Sci. **11**, 28 (1925) for the quantum analysis of this system.

[29] Hof, "Untersuchung über die Spektren von Kohlenoxyd und Kohlensäure," Dissertation, Basel (1914).

[30] Bair, Astrophys. J. **52**, 301 (1920).

He measured the wave-lengths of 100 bands, stretching from λ2068 to λ1335.[31] The bands are gradually fading out at this latter point, probably due to general absorption of some kind, and it seems apparent at the present time that the system runs further toward the short wave-lengths.

It is evident that the first two bands measured by Lyman (λλ2068.4 and 2047.0) are identical with the last two measured by Deslandres (λλ2066.8 and 2045.6) and that therefore all of the bands observed by Deslandres and by Lyman may be closely related. Very recently Duncan[32] has measured 14 of the strongest bands between λ2338 and λ2040. Duncan, however, as the writer[9] has pointed out, did not recognize these bands as a portion of the fourth positive group of carbon, and called them a seventh positive group of nitrogen.

A comparison of all available data seems to indicate that it is necessary to raise Deslandres' wave-lengths (in air) by 1.0A, in order to bring them into agreement with those of Bair and Duncan. These wave-lengths, reduced to vacuum then agree fairly well with those of Lyman (in vacuum) in the overlapping portion. The set of wave-lengths adopted in the present work and listed in Table II then consists essentially of Lyman's measurements for the wave-lengths *in vacuum* in the region λ2068 to λ1335, and of Deslandres' measurements, raised by 1.0A, for the wave-lengths *in air* in the region λ2632 to λ2090. In the reduction to vacuum, Kayser's "Tabelle der Schwingungszahlen" has been used. With the present experimental errors, the distinction between the Rowland and the I. A. system may be ignored.

The intensities, as given in column 3, are due to Lyman and to Deslandres, respectively. Because of the great extent of the system, these are not even qualitatively comparable, except for closely adjacent bands. Lyman marks a few strong bands as double, indicated by "*d*" in the intensity column and in Fig. 2. All the bands of this system are presumably double headed, due to a *Q* branch, as in the case of the Ångström CO bands. These two systems, according to the present theoretical interpretation to be discussed later, should have a similar fine structure.

Bair gives bands at λ2188 and λ2107.7, not listed by Deslandres. Duncan gives one of these (at λ2107.1), and also a band at λ2209.0 not listed by any other investigator. Of these three bands, only λ2107.1 finds a place in the system, as analyzed below. Other bands (or lines) not apparently belonging in the system are mentioned later.

[31] A photograph of the portion of this system between λ1335 and λ1880 is published by Lyman in Astrophys. J. **23,** 181 (1906) (1, Plate XI), and in Memoirs Amer. Acad. Arts **13,** 125 (1906) (Plate VII).

[32] Duncan, Astrophys. J. **62,** 155 (1925).

(*b*) Quantum Analysis

Deslandres has arranged the bands of nearly all his systems in sets called progressions. The quantum theory of band spectra has shown that these progressions consist of bands with a common lower (final) vibra-

TABLE II

Fourth positive group of carbon

1 λ	2 ν_{vac} (cm^{-1})	3 *I*	4 $n'-n''$	5 $O-C$ (cm^{-1})	1 λ	2 ν_{vac} (cm^{-1})	3 *I*	4 $n'-n''$	5 $O-C$ (cm^{-1})
2632.55	37,974.5	4	11–22	− 1	2068.4	48,346.5	8	4–11	+ 7
2600.0	38,450.0	6	10–21	− 3	2047.0	48,852.0	8	3–10	+ 5
2569.2	38,911.0	4	9–20	+ 9	2035.1	49,137.6	4	6–12	+ 6
			5–17?	− 7	2031.7	49,219.9	1	9–14?	+11
2557.8	39,084.4	2	12–22	+ 8	2026.4	49,348.6	7	2–9	+ 5
2539.7	39,362.9	4	8–19	+10	2012.6	49,687.0	8	5–11	+ 5
2525.1	39,590.5	4	11–21	+12	2007.2	49,820.6	5	1–8	−11
2511.8	39,800.1	6	7–18	+ 6	1991.0	50,226.0	1	4–10	+ 3
2493.7	40,089.0	4	10–20	+17	1970.1	50,758.8	8	3–9	+ 4
2485.2	40,226.1	4	6–17	− 2	1953.0	51,203.3	5		
2464.3	40,583.7	4	9–19	+28	1951.7	51.237.4	5		
2459.8	40,641.4	2	5–16	− 7	1950.4	51,271.5	4	2–8	− 6
2436.0	41,038.4	8	8–18	+ 6	1933.6	51,717.0	2	5–10?	−48
			4–15?	−24	1931.5	51,773.2	6	1–7	−18
2426.0	41,207.6	6	11–20	± 0	1918.2	52,132.2	7	4–9	± 0
2408.4	41,508.7	8	7–17	+10	1914.0	52,246.6	1	0–6?	−49
2395.0	41,740.9	6	10–19	+15				7–11?	−16
2382.5	41,959.9	8	6–16	+ 4	1898.0	52,687.0	10	3–8	− 2
2365.8	42,256.1	6	9–18	+12	1891.2	52,876.5	6	6–10	+ 3
2357.3	42,408.4	4	5–15	+ 4	1878.5	52,234.0	10d	2–7	− 3
2338.7	42,745.7	6	8–17	+ 9	1870.3	53,467.4	3	5–9	− 7
2333.5	42,840.9	2	4–14	− 1	1859.6	53,775.0	10d	1–6	− 1
			11–19	−20	1849.4	54,071.6	4	4–8	+ 7
2312.4	43,231.8	8	7–16	+ 3	1846.7	54,150.6	2	7–10	+ 5
2310.7	43.263.6	4	3–13	−10	1841.3	54,309.5	8	0–5	+ 3
2302.7	43,413.9	2	10–18	+ 8	1837.2	54.430.7	1		
2287.2	43,708.1	8	6–15	− 4	1830.1	54,641.8	9	3–7	− 6
			2–12?	+13	1825.7	54,773.5	7	6–9	− 8
2274.5	43,952.1	4	9–17	+10	1811.0	55,218.1	10d	2–6	− 4
			12–19?	−14	1804.9	55,404.7	8	5–8	− 2
2262.6	44,183.2	4	5–14	− 3	1801.9	55,497.0	2		
2247.7	44,476.1	4	8–16	+ 8	1792.6	55,784.9	10d	1–5	− 1
2238.8	44,652.9	4	4–13	+ 3	1785.1	56,019.3	6	4–7	− 5
2221.7	44,996.5	8	7–15	+11	1774.9	56,341.2	8d	0–4	± 0
2216.3	45,106.2	6	3–12	± 0	1747.3	57,231.2	7	2–5	− 1
			10–17	− 5	1743.5	57,355.9	3	5–7	−11
2209.0	45,255.2	1			1729.5	57,820.2	8d	1–4	− 1
2196.9	45,504.4	8	6–14	+11	1723.9	58.008.0	6	4–6	− 2
2195.0	45,543.8	6	2–11	− 8	1712.2	58,404.4	7	0–3	+ 2
2189.1	45,668.6	2	9–16	− 3	1705.3	58,640.7	6	3–5	− 1
2188	45,689				1698.8	58,865.1	1		
2173.3	45,998.5	8	5–13	+ 6	1688.5	59,224.2	1	2–4?	−43
			1–10?	+ 8	1685.3	59,336.6	1	5–6	−14
2162.6	46,226.1	8	8–15	+ 3	1669.9	59,883.8	6	1–3	+ 2
2150.9	46,477.5	8	4–12	− 5	1666.7	59,998.8	1	4–5	−20
2137.5	46,768.8	6	7–14	+ 3	1653.3	60,485.1	4	0–2	− 3
2128.8	46,959.9	2	3–11	− 4	1648.2	60,672.2	5	3–4	− 6
2113.7	47,295.4	8	6–13	− 5				6–6?	+13
2107.1	47,443.5	2	2–10	+ 8	1630.3	61,338.4	6	2–3	+10
			9–15?	+15				5-5	−23
2090.3	47,824.7	8	5–12	± 0	1629.6	61,364.7	3		

TABLE II (*continued*)

1 λ	2 ν_{vac} (cm^{-1})	3 I	4 $n'-n''$	5 $O-C$ (cm^{-1})	1 λ	2 ν_{vac} (cm^{-1})	3 I	4 $n'-n''$	5 $O-C$ (cm^{-1})
1623.4	61,599.1	1	10-8?	− 2	1463.7	68,320	3	4-1	+ 7
1615.1	61,915.7	2	7-6	−16	1452.4	68,851	3	6-2	± 0
			1-2?	−52				13-6	+ 4
1611.7	62,046.3	3	4-4	− 8	1447.0	69,108	1	3-0	+34
1603.3	62,371.4	1	9-7?	−19	1443.7	69,266	1	8-3	−11
1597.4	62,601.7	3	0-1	+ 2	1438.7	69,507	1		
1596.1	62,652.7	1	6-5	−15	1435.6	69,657	2	5-1	+ 2
			3-3?	−75	1426.1	70,121	3	7-2	− 3
1576.5	63,431.6	4	2-2	+18	1419.0	70,472	2	4-0	+22
			5-4?	−65				9-3	− 9
1559.3	64,131.3	5	1-1	+51	1414.0	70,721	1	11-4	− 4
			4-3	+16	1411.4	70,852	1	13-5	− 5
1545.1	64,720.7	3	0-0	−16	1409.0	70,972	2	6-1	+ 9
			6-4	+17	1405.5	71,149	1		
1542.2	64,842.4	5	3-2	+17	1404.0	71,225	1		
1534.2	65,180	2	8-5	− 1	1401.1	71,372	2	8-2	+ 9
1527.6	65,462	3	5-3	+ 5	1395.7	71,649	2	10-3	− 2
1526.0	65,531	2	2-1	+ 5	1392.2	71,829	1	5-0	+37
			10-6?	−14				12-4	+ 3
1520.4	65,772	1	12-7	−24	1386.4	72,129	1		
1515.7	65,976	3	7-4	− 1	1384.4	72,233	1	7-1	− 3
1510.7	66,194	2	1-0	−23	1378.1	72,564	2	9-2	− 3
			4-2	− 8	1374.1	72,775	2	11-3	−11
1506.8	66,366	2	9-5	−19	1371.8	72,897	2	13-4	+ 5
1497.8	66,764	3	6-3	− 1	1368.0	73,099	1	6-0	− 1
1493.8	66,943	3	3-1	+ 7	1361.3	73,459	2	8-1	−16
1488.0	67,204	2	8-4	−12	1356.1	73,741	2	10-2	+ 4
1480.9	67,526	2	5-2	−17	1353.6	73,877	1	12-3	−10
1478.0	67,659	2	2-0	− 4	1343.0	74,460	1	7-0?	+85
1475.4	67,778	1	12-6	− 2	1339.0	74,683	1	9-1	+ 4
1473.0	67,889	1	14-7	− 5	1335.0	74,906	1	11-2	+34

tional level, (here designated n' progressions), or of a common upper (initial) level, (here designated n'' progressions). It is further found that Deslandres' n *usually* refers to the lower level, so that his first progressions, $[f(n)]$, are usually n'' progressions, while his second progressions $[f(p)]$ are usually n' progressions.[33] There are however exceptions, as in the case of the first positive group of nitrogen. If the "origin" of each band, as defined by the quantum theory, is used, the various first or the various second progressions should differ only in the constant term. It is however ordinarily necessary at the present time to use data for the heads, and therefore the various first or second progressions are not quite identical, although the variations may easily be less than the experimental error.

In the case of this fourth group of carbon, Deslandres arranged the bands in five progressions, designated I to V, but the numerical relations, on this interpretation, are quite unusual, as the writer[7] has noted. Later

[33] The numbering of n' and n'' is quite different from that of n and p, and always runs in the opposite direction.

the thought occurred that in this one case, Deslandres' progressions were probably actually sequences, i.e., sets of bands having a common value of $n''-n'$, and usually much more closely spaced than the bands of a progression. With this new interpretation, it was possible to obtain progressions having the expected relations. Now Lyman[12] had arranged 28 bands out of the 100 measured by him in six series (designated VI to XI) similar to those formed by Deslandres. He called these 28 bands the "fifth positive group of carbon." An extrapolation of the new progressions, as arranged by the writer, led directly to the bands of this fifth group, and showed that Lyman's progressions also were actually sequences. Further extrapolation resulted in the identification of practically all the remaining bands as parts of one great system which it seems best to designate as the fourth positive group of carbon. The true quantum designations ($n'-n''$), giving the upper and lower vibrational quantum numbers respectively, appear in column 4 of Table II. As can be seen, only a dozen bands remain unassigned. These latter include the two *strong* bands λλ1953.0 and 1951.7. These two bands I have however found on one of Professor Hopfield's spectrograms, and are, I believe, really a double *line*, of unknown origin. All of the remaining unassigned bands are extremely weak, with the exception of λ1801.9 (2), and λ1629.6 (3), and all *may* be lines.

On the other hand, many of the measured heads seem to represent the blending of two or more bands. Such matters can best be discussed by considering the general intensity distribution of the system, as shown in Fig. 2. In this $n'n''$ diagram merely the intensities are listed. When a band is believed to be the superposition of two, it is starred. The details may be obtained from Table II. The broken line in Fig. 2 marks the division of Deslandres' and Lyman's data. The distribution of intensity shown in this figure is now known to be typical of a fairly large change in the moment of inertia accompanying the emission of the bands.[34] Condon,[35] in his extension of Franck's[36] mechanical explanation of the intensity distribution, has obtained a satisfactory quantitative agreement for this particular system. The expected symmetry of the distribution indicates however that the true relative intensity of the bands near the short wave-length limit is greater than shown, and that the system runs still further to the shorter wave-lengths.

Because of the relatively large general experimental errors, and the many blended bands, it is difficult to obtain a trustworthy formula for

[34] See "Report," Chap. IV, Section 4, for detailed discussion.
[35] Condon, Phys. Rev. **27**, 640 (A) (1926). Detailed article in Phys. Rev. **28**, (1926).
[36] Franck, Trans. Faraday Soc. **21**, Part 3 (1925).

this band system. That previously published by the writer[9] was based upon an analysis of the frequency *differences* of the successive bands in the progressions, since there was no certainty that the absolute wave-lengths of the various investigators were consistent. A more searching examination of this question, made recently, indicates that all of the

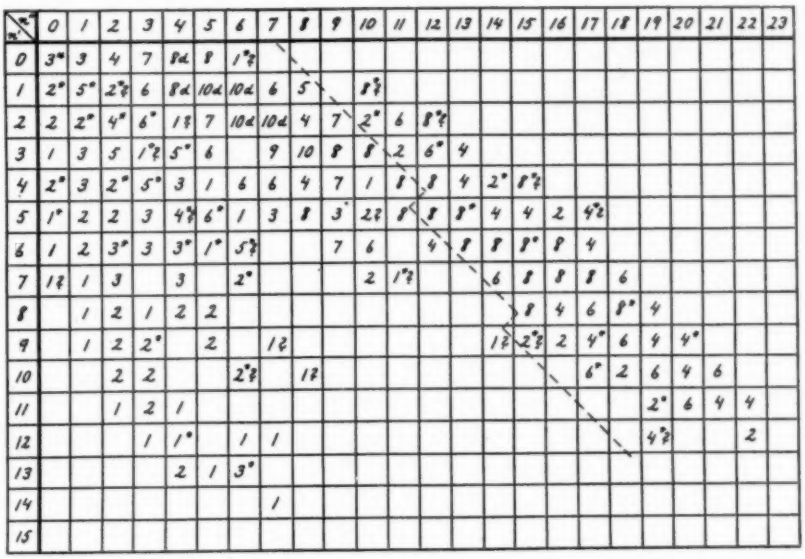

Fig. 2. Distribution of intensity in the fourth positive group of carbon. Starred numbers refer to blended bands, as given in Table II.

wave-lengths listed in Table II are consistent within the limits of experimental error, and that it is possible to obtain a simple formula giving no noticeable trend in the residuals. This formula, which differs slightly from that previously published, is[37]

$$\nu = 64{,}737 + (1497.28n' - 17.24n'^2) - (2149.74n'' - 12.703n''^2) \quad (1)$$

The residuals for every band of the system, calculated according to this revised formula, are listed in column 5 of Table II. Some of these are rather large, but in a majority of such cases the error is obviously due to the difficulties of measurement caused by overlapping bands. In a few cases there seems to be an actual error of setting. The writer hopes to obtain in the near future better data for this system, and to examine all apparent discrepancies.

[37] The old formula is $64{,}721 + (1499.28n' - 17.24n'^2) - (2147.74n'' - 12.703n''^2)$. The changes were made of exactly two units merely for convenience. The probable error in the constants 2149.74 and 1497.28 is several tenths of a unit.

An important point in connection with Eq. (1) is the fact that the vibrational energy of both the initial and the final state can be represented by a second degree equation, (i.e., that the $\omega^n : n$ curve giving the frequency of vibration as a function of n is strictly linear). Considering the large range of values of n as shown in Fig. 2, this is a surprising result. More accurate data may show that the $\omega^n : n$ curves deviate slightly from linearity, but the deviation, if it exists, must be very small. It can scarcely change the value of the heat of dissociation D, as calculated by Birge and Sponer,[19] by an appreciable amount. The new value of D given by Eq. (1) is only 0.02 volts greater than the older value.

The most important result of the quantum analysis of this band system was the discovery that the n' progression for $n''=0$ was identical with the bands found by Leifson[13] in the absorption spectrum of cold carbon monoxide. Leifson's measured values average 1.3 ± 0.2A higher than the theoretical values given by Eq. (1). But Leifson's setting is on the center of the narrow, fairly symmetrical double band characteristic of low temperature (like the infra-red bands) while the equation applies to the violet edge (head) of the high temperature band. The discrepancy is therefore in the correct direction and apparently of the expected amount. Leifson's measured absorption bands begin at $0-0$ and run to $11-0$, being limited only by the transparency of his fluorite window, while Lyman's emission bands run only to $7-0$. Leifson's last band at $\lambda 1264.6$ is therefore an extension of the system to the shorter wave-lengths. His bands should occupy the first column of Fig. 2, but are not shown.

This correlation of Leifson's data with that of Lyman proves beyond question that the general quantum arrangement shown in Fig. 2 is correct, and also proves that these bands are due to neutral carbon monoxide and that the lower electronic state of this system is the normal state of the molecule. The basis for the complete set of energy levels of CO was thus established, as discussed by the writer,[9] and reviewed in the introduction of the present paper.

If the present interpretation is correct, the lower vibrational levels of the fourth positive group are merely those levels which are concerned with the vibration-rotation bands of the near infra-red. Three such bands are known ($1-0$, $2-0$, and $3-0$) at 4.67μ, 2.35μ, and 1.573μ, as measured by Schaefer and Thomas.[38] Using Eq. (1), we *calculate* for these bands the values 4.679μ, 2.354μ, and 1.578μ. This is the first molecule for which the available data make possible a correlation of electronic bands in the visible and ultra-violet with vibration-rotation

[38] Schaefer and Thomas, Zeits. f. Physik. **12**, 330 (1923).

bands in the near infra-red. The above *quantitative* agreement is a real confirmation of the general quantum interpretation of band structure.

The Ångström CO Bands

A further result of the above analysis of the fourth positive group was the discovery that the Ångström CO bands could be so interpreted as to have as a lower level, the upper level of this system. There can scarcely be any doubt as to the validity of this conclusion, but because of one puzzling irregularity a rather detailed discussion seems advisable.

The older data for the Ångström CO bands are listed on pp. 227–8 of Kayser, Vol. V. These bands, degraded to the violet, were originally measured by Ångström and Thalén,[39] who recorded 29 band heads between λ6854 and λ4123. Seven of them were labelled as an "*a*" series, and except for the last one (λ4209), these bands are now interpreted as constituting the n'' progression for $n'=0$. Seven other bands were

TABLE III

Ångström bands of CO

1 $n'-n''$	2 ν_{calc}	3 Loos	4 Hulthén	5 M. S. P.	6 Jassé	7 Watts	8 A. & T.	9 *I.*
0–0	22,156.6	+5.8			+6.2	+6.2	+8.7	4
0–1	20,676.6	−1.0	−1.3			−0.7	+1.0	4
0–2	19,231.0	+1.2	+1.2			+1.2	+0.7	5
0–3	17,819.9	+0.3	±0.0	+3.6		+0.2	+4.3	5
0–4	16,443.3			−1.9		+2.8	+1.4	4
0–5	15,101.2			−0.3			−7.2	3
0–6	13,793.6			+3.3				
1–0	24,237.6	+8.2			+6.4	+8.6	−44.8	3
1–1	22,757.6	−0.5	−1.1			−0.5	−12.4	3
1–2	21,312.0						−33.7	2
1–3	19,900.9						+28.6	2
1–4	18,524.3						−6.8	3
1–5	17,182.2						+0.2	3
1–6	15,874.6						−5.2	2
2–0	26,164.6							
2–1	24,684.6							
2–2	23,239.0						+3.3	1
2–3	21,827.9						−6.1	1
2–4	20,451.3							
2–5	19,109.2							
2–6	17,801.6							

labelled "*b*" bands, and these constitute the n'' progression for $n'=1$. It is very doubtful if any of the remaining heads are anything more than accidental clusters of lines. This is evident from the photograph given in Konen "Atlas der Emissionsspektren," No. 269 and 279[40] where only

[39] Ångström and Thalén, Nova acta Reg. Soc. sc. Upsal. (3), 9 (1875).

[40] The scale on 279 should be shifted 100A to the right.

the a and b bands appear, and from the fact that no subsequent investigator has measured any but these a and b bands. However, in Table III, the possible bands 2–2 and 2–3 of the $n'=2$ progression are listed, and are used in deriving the constants of Eq. (3) ahead. Watts and Wilkinson[41] later measured five of the a bands, and two of the b bands. Their measurements agree well with those of subsequent investigators, and show that the Ångström and Thalén wave-lengths should be raised 1.5A. This change has been made in obtaining the figures of Table III. The first fine structure analysis was made by Loos,[42] who incidentally measured with great accuracy the heads of the bands later given by Watts and Wilkinson, with the exception of λ6079 (0–4). All of these measurements are in the Rowland system, and are listed in Kayser's Handbuch.

Hulthén[43] made the first quantum analysis of these bands,—in fact this work constitutes the first accurate verification of the combination principle as applied to band spectra, and is consequently of the highest importance. His measurements give data for the heads and also for the origins of the four bands λλ5610, 5198, 4835, and 4393. His assignment of quantum numbers (n and p) was however incorrect, the true n' and n'' being given by

$$n'=n-2, \qquad n''=p+1 \tag{2}$$

Hulthén stated that the strong a band λ4511 had a different structure from the others, and hence did not belong to the system. This exclusion carries with it the strong b band λ4123. But very recently Jassé[44] has shown that the λ4511 band *does* have a structure similar to the others (a singlet P, Q, and R branch), but has in addition extra branches called P' and R'. The writer[45] finds that the moment of inertia calculated from the P and R branches of the λ4511 band (the 0–0 band) is entirely consistent with the value obtained from Hulthén's data. The extra P' and R' branches yield an "origin" identical with that for the usual branches, but a moment of inertia about $\frac{3}{4}$ as large. The origin and interpretation of these additional branches is as yet entirely a mystery and it may be the case that they are spurious.

Jassé analyzed also the λ4123 (1–0) band, and the moment of inertia evaluated from this band also agrees with Hulthén's data. It therefore seems evident that these two bands form a part of the system. Both of them are however displaced 6 to 8 wave numbers from the expected

[41] Watts and Wilkinson, Phil. Mag. (6) **12**, 581 (1906).
[42] Loos, Zeits. wiss. Phot. **1**, 151 (1903).
[43] Hulthén, Ann. d. Physik **71**, 41 (1923).
[44] Jassé, Compt. rendus. **182**, 692 (1926).
[45] "Report," Chap. IV, Section 7, note (g).

position, as indicated by the residuals of Table III, and this displacement is a most surprising fact. It occurs regardless of whether heads or origins are used, and is in fact slightly larger for the latter, as shown later. (Table III uses data for heads.)

The only additional measurements are those of McLennan, Smith, and Peters.[46] These cover only four a bands (0–3 to 0–6) but are more accurate than the older Ångström and Thalén measurements and were of real assistance to the writer in verifying the identity of the final state of the Ångström bands with the initial state of the fourth positive group. In Eq. (3) this identity is assumed, the $f(n'')$ being taken arbitrarily as the $f(n')$ of Eq. (1). The residuals listed in Table III indicate that this assumption is entirely justified, with the exception of the strange displacement of the 0–0 and 1–0 bands already noted. In Table III there are given in column 1 the $n'-n''$ assignments, and in column 2 the frequency in vacuum, in the I.A. system for the heads of the bands, calculated from the equation[47]

$$\nu = 22{,}156.6 + (2158n' - 76n'^2) - (1497.28n'' - 17.2n''^2) \qquad (3)$$

The next six columns give the residuals in cm^{-1} for the data of Loos, Hulthén, McLennan Smith and Peters, Jassé, Watts and Wilkinson, and Ångström and Thalén, respectively. Where necessary the Rowland measurements have been reduced to I.A., and then all to vacuum. The Ångström and Thalén measurements have been raised 1.5A, as stated. The last column gives the intensities according to Ångström and Thalén.

The progression of a bands (0–0 to 0–6) differs from the b bands (1–0 to 1–6) by 2081 cm^{-1}. This is the only figure for the $f(n')$ that is at all certain. The $f(n')$ given in Eq. (3) is derived from the assumed identity of the 2–2 and 2–3 bands. The true head of the 0–0 band is at 22,162.8 cm^{-1} according to Jassé (instead of 22,156.6 as calculated) and the origin is at 22,172.0. The distance from head to origin is thus 9.2, while for the next four a bands, Hulthén measures this same difference as 7.1, 7.3, 7.4, and 7.2. The discrepancy for the 0–0 band is again surprising.

It should be pointed out in this connection that there is no violation of the combination principle in the position of the 0–0 and 1–0 bands, but merely an observed spacing of the two vibrational energy levels $n''=0$ and 1, greater than that obtained by extrapolation of a *linear* $\omega^n : n$ curve. In fact, with the data by Hulthén for the λ4835 (0–1) and

[46] McLennan, Smith and Peters, Trans. R. S. Canada **19**, 39 (1925).

[47] Mecke (Phys. Zeits. **26**, 217 (1925)) has adopted the same quantum assignments as those given here, and has given as the correct representation of the three a band *origins* measured by Hulthén, $\nu = 22{,}154.6 - (1487.05n'' - 14.85n''^2)$. This formula is however unsatisfactory for the more extensive data used here.

λ4393 (1–1) bands, and by Jassé for the λ4511 (0–0) and λ4123 (1–0) bands, it is possible to test the combination principle, line by line, and to evaluate the frequency of vibration as a function of the nuclear quantum number $m(=j-0.5)$. In this case the frequency of vibration corresponds to $n=\frac{1}{2}$, since the interval is between $n=0$ and 1. The theoretical expression is[48]

$$\omega_m^n=\omega_0{}^n(1-\gamma m^2) \tag{4}$$

and the actual results I find to be

$$\omega'=2081.5(1-1.29\times10^{-5}m^2) \tag{5}$$

for the initial state, from the data of Hulthén, and 2082.3 into the same parenthesis, from the data of Jassé. There is thus a uniform discrepancy of 0.8 cm^{-1} in the data of the two observers, or else a violation of the combination principle by just this amount. The former alternative is doubtless the correct one. For the final state I obtain

$$\omega''=1488.6(1-2.62\times10^{-5}m^2) \tag{6}$$

from the 0–1 and 0–0 bands, and 1489.4 into the same parenthesis from the 1–1 and 1–0 bands. The *relative* wave-lengths of *each* investigator are evidently quite accurate, for the average residual calculated from Eq. (5) is less than 0.1 cm^{-1} for each. But in Eq. (6) the residuals are much larger, thus proving that discrepancies really exist between the data of the two observers. It may be noted in conclusion that the 1488.6 (or 1489.4) of Eq. (6) for the final state is to be compared with the expected value of 1480.04 given by Eq. (3), while the 2081.5 (or 2082.3) of Eq. (5) for the initial state is to be compared to 2081.0. Since Eq. (3) refers to the heads, and Eqs. (5) and (6) to the origins, the agreement is very good for the initial state interval. The disagreement for the final state is the surprising fact already noted and constitutes apparently a *vibrational* "perturbation."

The Third Positive Group of Carbon, and the Cameron Bands

The third positive group of carbon, extending from λ3825 to λ2295, was first measured by Deslandres,[11] and consists of three progressions which must be interpreted[49] as n'' progressions corresponding to $n'=0$, 1, and 4. The measurements are given on page 233 of Kayser vol. V. Wolter[50] later made a partial study of the fine structure, and concluded

[48] See "Report," Chap. IV, Eq. (51).
[49] See Birge, reference (7), and Johnson, reference (15).
[50] Wolter, Zeits. wiss. Phot. 9, 361 (1911).

that only the progression which we have called $n'=0$ was real. This consists of six bands degraded toward the violet, whose heads, using the data by Wolter, are given by

$$\nu=\nu_e-(1724.78n''-14.47n''^2) \tag{7}$$

where ν_e is six-fold, the six heads of the 0–0 band lying between 35,287.6 cm^{-1} and 35,390.4 cm^{-1}. Each band, in addition to the six-fold head, is characterized by a curious repeated rise and fall of intensity. This appears clearly on Wolter's published photograph of the λ2977 (0–1) band (reproduced also on page 211 of Konen "Das Leuchten der Gase und Dämpfe"). The other two progressions of Deslandres, according to Wolter, are merely chance clusters of lines in one of these secondary intensity maxima. Duffendack and Fox[18] have however recently obtained the so-called $n'=4$ progression at a different critical voltage from the $n'=0$ progression, and they consider it to be the $n'=0$ progression of a *new* system (called 3A). On this interpretation each system consists in all probability merely of the n'' progression for $n'=0$, the 3A system being given by

$$\nu=43,556-(1724.78n''-14.47n''^2) \tag{8}$$

where the constant term refers to the least refrangible of the six heads. Since only the $n'=0$ progression of this new system is known, we cannot evaluate the frequency of vibration for the initial state. The same situation is true for the third positive group, if Wolter's conclusion regarding the $n'=1$ progression is correct. Assuming however this progression to exist, the Deslandres[11] data give 2214 cm^{-1} as the single known interval. The value 2264 previously published by the writer[19] (or 2258.5 as given by Johnson[15]) was obtained from the assumed reality of the $n'=4$ progression.

Meanwhile Johnson[15] had given

$$1728.2n-14.6n^2 \tag{9}$$

as the $f(n)$ representing both the final state of this third positive group and the initial state of the newly discovered Cameron[16] bands. Now Deslandres' data for the third positive group, used by Johnson, give

$$1731.25n-15.39n^2 \tag{10}$$

while Cameron's data for his new bands give

$$1727.3n-14.35n^2 \tag{11}$$

but all of these discrepancies are easily within the limits of error.

Moreover, Johnson finds that the Cameron bands have a five-fold head and he gives figures indicating that the separations are the same as those occurring for the third positive group, providing the second head of this latter group is omitted. The situation is however not as simple as this. The theory to be discussed later in the present paper predicts that the common level associated with these two band systems should be triple. If each band has a Q branch, as is to be expected from various considerations, there will be apparently six heads, three of them being the heads of the three Q branches, defining the triple origin, while the other three are the true heads of the bands (turning points of R or P branches). Thus if the six heads are numbered in the direction of degradation of the bands, then in the case of *both* systems, the second, fourth, and sixth heads are the Q branch heads, and the respective separations (defining $4\text{–}2=A$, $6\text{–}4=B$) give the intervals A and B of the triple electronic level, A lying above B, on the energy diagram, Fig. 1. The value of A and of B must be the same for both systems. It is however unnecessary that the other intervals shall be the same. Thus the identity of all intervals, as quoted by Johnson, is if true merely a coincidence, according to the present interpretation.

The details are as follows. If Wolter's data for the third positive group are used, the five intervals (2–1, 3–2, 4–3, etc.) are 11.86, 17.74, 19.98, 19.93, and 27.77. Johnson, from his own plates, gives 8.8, 27.6, 17.4, 17.8, and 29.6, and there is thus a considerable discrepancy. Cameron's published wave-lengths for the other system yield for the unweighted values of the intervals, 37.53, 18.80, 18.00, and 29.33 cm^{-1}. Johnson, however, using the same data, quotes 37.8, 18.3, 17.2, and 29.8 cm^{-1}. It is evident here that if the Cameron bands also have six-fold heads, it must be the second head which has not been measured. The value of B from the third positive group, using Wolter's data, is 47.70 cm^{-1}, or using Johnson's data is 47.4. Its value from the Cameron bands is 48.13. The agreement is well within the limits of error. The value of A from the third group, using Wolter's data, is 37.72, or using Johnson's data, is 45.0, a wide discrepancy. We cannot obtain this interval from the Cameron bands, since the second head has apparently not been measured. If however the value of A, obtained from the third group, is assumed for the Cameron bands, one can calculate the 1–2 and 2–3 intervals, and the results are more reasonable if Johnson's value of 45.0 is taken.

The above relations are consistent with the theory that we have here a triple electronic level which is common to the third positive group and the Cameron bands. There is however one possible objection. The three intervals 1–2, 3–4, and 5–6, giving the separation of each band

head from its origin, while not necessarily the same for the two systems, are normally roughly constant in the same system. But these intervals are 8.8, 17.4, and 29.6 for the third group (Johnson's data), and 10.53, 18.00 and 29.33 for the Cameron bands, on the basis of 45.0 for the A interval. The variation from 8.8 to 29.6 and from 10.5 to 29.3 is quite unusual, but Professor Mulliken (private communication) reports a similar variation for the red CN bands.

It is not possible, from the twelve measured Cameron bands, to give the n'' numbering for this system, for the sequence $n''-n'=1$ is faintly present, but not measured, while the zero sequence is not observed at all. However the six final state intervals actually measured agree with those resulting from the writer's analysis of the fourth positive group so well that Johnson immediately assumed that the two systems had a common final state, and that the Cameron bands thus constituted a second "resonance" system of neutral CO. The actual $f(n'')$ found by Johnson is, in fact,

$$2151.1n''-12.7n''^2 \tag{12}$$

while, using the better data for the fourth group and for the third group, the whole Cameron system should be given by

$$\nu=\nu_e+(1724.78n'-14.47n'^2)-(2149.74n''-12.70n''^2) \tag{13}$$

where $\nu_e=48{,}529.9$, 48,492.4, 48,473.6, 48,455.6, and 48,426.3. The expected n' progression, for $n''=0$, does not appear on Leifson's absorption plates of carbon monoxide, but this is not necessarily an objection to the above interpretation, since the atmospheric bands of oxygen, for instance, require a considerable quantity of absorbing gas in order to be detected. Moreover, Hopfield (unpublished work) has now found the $n''=0$ progression of Cameron bands in absorption in carbon monoxide.

Discussion

Generalizing previous tentative suggestions by Mulliken and others, the writer[14] has assumed that "the energy levels associated with the valence electrons of molecules agree in all essential aspects with those associated with the valence electrons of atoms." In this same reference the previous evidence on this point is briefly summarized, and some new evidence is presented. Some of the relations just discussed in connection with the spectrum of carbon monoxide form the most significant portion of this new evidence. Taking the above generalization as a basis for action, Mulliken[51] has very recently worked out extensive systematic

[51] Mulliken, Proc. Nat. Acad. Sci. **12**, 144, 151, 158, and 338 (1926); Phys. Rev. **28**, 481 (1926), Phys. Rev. **28**, 1202, (1926).

relations in band spectra, and has presented the results in a series of remarkable papers. In the present paper there is hardly space to give a detailed critical discussion of these new developments. A brief summary of certain points is however advisable.

It has commonly been assumed that there are two main types of diatomic molecules,—one consisting of loosely bound atoms (low heat of dissociation) and the other of firmly bound atoms (high heat of dissociation). It has been thought that the first type consisted merely of two atoms held together by mutual polarization effects (secondary, or van der Waals forces), the quantization of the various electronic orbits being identical with that of the two atoms when entirely separate. It should be possible to separate such a molecule continuously (adiabatically) into its constituent atoms, not only by electron impact, but also by absorption of light. In the case of iodine this latter process is actually observed in the n' progression of bands which runs to a definite head at 20,020 cm^{-1}. Dymond[52] has proved that this point corresponds to dissociation of the molecule.

On the other hand, it has been supposed that in the case of firmly bound molecules like O_2, N_2, CO, etc., certain electrons are in quantum orbits different from those in the atoms. Such orbits may possibly encircle both nuclei. On such a basis, Mulliken adopted the Lewis-Langmuir idea of octets in the N_2, CO, and NO molecules. On this interpretation, each of these molecules has four K electrons (each atom with its usual two), while the remaining electrons are arranged in some sort of a group of eight, with two (for N_2 and CO) or three (for NO) extra electrons. These extra electrons are assumed more loosely bound and hence may be termed the valence electrons of the molecule. On such an assumption N_2 and CO may be correlated with the two-valent atom Mg, since this has two K electrons, a group of eight L electrons, and two valence electrons. Similarly NO is correlated with Al.

Now it has been shown that the character of the spectral formulas known to hold true for atoms (Rydberg, Ritz etc.) is due to the essentially constant penetration of an electron into a cluster of electronic charges, in a series of orbits of the same angular momentum (k) but varying total momentum (n). If the electronic orbits in molecules are quantized in a manner at all similar to those in atoms, we should therefore expect that the spacing of the electronic energy levels associated with the loose-bound ("valence") electrons in molecules should follow at least approximately the same law as is found in the case of atoms. Previous work by

[52] Dymond, Zeits. f. Physik **34**, 553 (1925).

Mulliken, Mecke, and Hulthén has shown that the molecular levels have a multiplicity quite similar to that found in atoms. The very recent work of Mulliken has been devoted mainly to assigning an inner quantum number j_a to each electronic energy level of the molecule, using precisely the same values as for the "corresponding" atom, on Sommerfeld's interpretation, and then correlating each j_a with the observed fine structure of the accompanying bands. This correlation, which has been very successful, gives a new basis for the correctness of the j_a values which it is not possible to obtain from a study of atomic structure.

The preceding sections of this paper give the experimental data necessary for the construction of a series of electronic energy levels for CO. To be accurate one should use in each case the origin of the 0–0 band. This however is unknown, except for the Ångström bands. For the sake of consistency we therefore in all cases use the head of the 0–0 band. The difference is immaterial for the present discussion. Beginning then with the normal state of the molecule (level X of Fig. 1) as the zero energy level, the initial state of the fourth positive group (level A of Fig. 1) is, by Eq. (1), 64,737 cm^{-1} (=7.995 volts[53]) while the initial state of the Cameron bands (level a) is, by Eq. (13) 48,426.3 to 48,529.9 cm^{-1} (=5.981 to 5.994 volts). Then from Eq. (3) the initial level of the Ångström bands (level B) is 86,894 cm^{-1} (10.732 volts), while from Eqs. (7) and (13), the best value for the initial state of the third positive group (level b) is 83,817.1 cm^{-1} (=10.352 volts). Finally, from Eqs. (8) and (13) we obtain 92,086 cm^{-1} (=11.374 volts) for the initial state of the new 3A bands of Duffendack and Fox[18] (level c). All of these values are listed in columns 3 and 4 of Table I.

Now in order to compare the law of spacing of electronic energy levels in molecules with that found in atoms, we need the "term" value of the various energy levels. This in turn requires a knowledge of the ionization potential of the molecule. Fortunately carbon monoxide is one of the very few molecules for which a fairly accurate value is known, the best direct measurements giving 14.1 and 14.3 volts[54] while from Duncan's measurement of the excitation potential of the first negative group of carbon,[55] one obtains 14.2 ± 0.3 volts (=114,966 cm^{-1}). Each "term" is then obtained from $114{,}966 - x$, where x is the cm^{-1} value of the level as previously listed. These values are given in column 5 of Table I. The *denominator* of each term is given by $D = \sqrt{\nu/R}$ where ν is the term

[53] 1 volt = 8096.2 cm^{-1}, according to recent data. See Birge, Science, **64**, 180 (1926).
[54] See page 123, Report by Compton and Mohler on "Critical Potentials."
[55] See Birge, reference (9).

value and $R = 109{,}678$ cm^{-1}. The results are listed in column 6, Table I. In the simple Rydberg formula the denominators differ by unity. The denominators first obtained by the writer,[14] for the levels X, A, and B, have the values 0.98 ± 0.02, 1.48 ± 0.10, and 1.98 ± 0.15, assuming 0.3 volts probable error in the ionization potential value.

By comparison with the term scheme of Mg (see Fig. 1) this immediately suggested that the true designations are $1\,{}^1S$, $1\,{}^1P$, and $2\,{}^1S$, using the nomenclature of Russell and Saunders. The Ångström CO bands consist merely of three branches (P, Q, and R) of strictly single lines. In this respect they correspond to the "single-line" series of atomic spectra, and by analogy we may conclude that the two levels concerned with this system also are single. This is in agreement with the designations just given. Similarly we may *predict* that the fourth positive group of carbon also will be found to consist of P, Q, and R branch bands, with the individual lines strictly single.

By similar analogy with Mg, it is probable that the new a and b levels of Johnson[15] are respectively ${}^3P$ and ${}^3S$ levels. This was noticed immediately by Mulliken and by the writer, as noted in the introduction. The evidence concerning the multiplicity of the a level has already been discussed, and we may assume provisionally that it is triple, even though there is still some uncertainty as to this. On this assumption, the triplet separations are approximately 45 and 48 cm^{-1} (A and B of the previous discussion) as compared to 41 and 20 for the corresponding level in Mg. In the case of N_2, the writer has interpreted the first positive group in such a way as to give 20 and 40 for the corresponding intervals, i.e., the molecular level is "inverted." Until this nitrogen system has been actually analyzed in respect to its fine structure, such a conclusion[56] must be regarded as merely tentative.

The assumption that the initial level of the Cameron bands is triple, while the initial level of the fourth positive group is single,—the common final level of both systems being single,—may be the explanation of the faintness of the Cameron bands in emission,[16] and the failure until recently to get them in absorption. For, as Professor H. N. Russell has reminded the writer, transitions between levels of varying multiplicity are very improbable in the case of light atoms, although quite the reverse is true for heavy atoms. Now CO is a molecule composed of two relatively light atoms, and if the same rule applies to molecules, the relation is quite as expected.

[56] Based on the spacing of the strong first, second, and fourth heads of the first positive group of nitrogen. It may be noted that Hund, in his important paper on the structure of molecules (Zeits. f. Physik **36**, 657 (1926)) predicts that the multiple levels in molecules should be *equidistant*.

The b level is apparently single, as it should be. Because of the crowding together of the levels, near the ionization potential, it is not possible to identify the new c level of Duffendack and Fox[18] with any certainty. Johnson has suggested that it is another ^3P level. The denominators (1.28 and 2.19) do not however favor this assumption and by comparison with Mg, it seems more likely that it is a ^3D level. (Compare Fig. 1, where these analogies with Mg are indicated by broken lines.) By making such an identification, all of the transitions for neutral CO obey the selective principle ($\Delta k = \pm 1$) of line spectra. This rule is apparently violated in certain molecules (CN, NO, and certainly BO and CO^+), but we do not know yet whether such violations are the exception or not, and I think it is at least significant that in the case of CO, where the analogy with a given atom is fairly complete, the rule is obeyed. The same situation is true in the case of the helium molecule, according to the analysis of Mulliken[57], but here we have undoubtedly merely two slightly distorted helium atoms, and might expect the atomic laws to apply. On the other hand, Hund's[56] theoretical analysis indicates that in molecules the transitions $\Delta k = 0, \pm 1$, are allowed.

In the case of CO^+, the analogy with Mg^+ is very good, as far as the multiplicity is concerned.[58] The A' level of Fig. 1 is double, with spacing 126 cm^{-1}, compared to 91.5 for the first ^2P level of Mg^+, while the X' and B' (^2S) levels are single, if as Blackburn[28] believes, the lines of the first negative group of carbon are strictly single. If the B' level is ^2S and if the Rydberg formula is true, the ionization potential of CO^+ is only 10.7 volts, placing this level at 24.9 volts on the Fig. 1 diagram (level X''). This point will be considered more at length in a separate paper on CO^+.

The energy levels for CO^+, plotted in Fig. 1, and given in Table I, are evaluated from the constants previously published by the writer.[7] In this case, values are known for the true origins of the comet-tail bands ($\nu_e = 20{,}472$ and $20{,}346$ cm^{-1}) and of the first negative group of carbon ($\nu_e = 45{,}638$ cm^{-1}) and these have been used for the calculation. Table I contains finally, in column 7, the frequency of vibration, ω'', for each of the electronic levels of CO and CO^+. It was at first believed that the relative values of ω'' could be used as a criterion for the identity of the various states. Thus all S states, in molecules like CO, have

[57] Mulliken, Proc. Nat. Acad. Sci. **12**, 158 (1926).

[58] See Birge[14] and contained references.

roughly the same value of ω'', while the P states have a smaller value. If this were a general rule, it should furnish valuable evidence regarding molecular structure, as was pointed out by the writer.[14] Recent work by Jenkins, Barton and Mulliken[59] on NO seems to indicate however that such a criterion is quite untrustworthy, and hence the theoretical conclusions based on it must likewise be uncertain.

Conclusion

The present paper has been concerned primarily with the experimental data for the band spectra of carbon monoxide. By a suitable analysis of these data, the general energy level scheme of Fig. 1 and Table I has been obtained. There can be no question as to the qualitative correctness of this scheme. The actual energy values of the various levels may be in error as follows. For the levels a, A, b, B, and c, of neutral CO, the error arises from the use of the head of a band in place of the origin, but the entire discrepancy for any level is probably less than 100 cm^{-1}. The relative position of the levels of CO^+, since these are given in terms of the true origins, is very accurate. On the other hand, the energy value of level X', and hence of all the CO^+ levels relative to the CO levels is uncertain to possibly 0.3 volts (2430 cm^{-1}), and the "term" values of the CO levels have the same uncertainty.

The energy scheme is thus established, but the correlation of the various levels with levels of the Mg atom is of course still a pure assumption. This correlation has been merely sketched in the present paper, with no attempt at critical discussion.

Note added in proof. Duffendack and Fox (Science **64,** 277, Sept. 17 (1926)) have recently obtained from data on excitation potentials striking confirmation of the quantum analysis of the CO and CO^+ band systems made previously by Birge[7,9,24] and Johnson.[17] The 0–0 band of the third positive group is emitted at a minimum voltage of 10.2, compared to 10.35 volts for level b, as given in Table I. Similarly levels B, c, A' and B' are placed at 10.7, 11.1, 16.9 and 20.0 volts, compared to the values 10.73, 11.37, 16.72 and 19.84 volts, of Table I. The only discrepancy is in the case of the combination bands of CO^+, which Duffendack and Fox find at 22.9 volts, compared to the calculated value of 19.84 volts. As a result they assume that these bands are due to a transition from a higher (C') level to the B' level, instead of from B' to A', and they remark "This system contains so few bands that its

[59] Mulliken, private communication.

relation to others can not be determined with certainty by analysis." This, however, is apparently not the case. There are six bands in the system and each fits unambiguously into the $B'-A'$ transition.

Still more recently, Ann B. Hepburn (Nov. 1926 meeting, Amer. Phys. Soc.) has obtained, in a similar way, data in complete agreement with the values in Table I, *including* the combination bands of CO^+.

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August 21, 1926.

A THEORY OF INTENSITY DISTRIBUTION IN BAND SYSTEMS*

By Edward Condon

Abstract

A theory of the relative intensity of the various bands in a system of electronic bands is developed by an extension of an idea used by Franck in discussing the dissociation of molecules by light absorption. The theory predicts the existence of two especially favored values of the change in the vibrational quantum numbers, in accord with the empirical facts as discussed by Birge.

A means of calculating the intensity distribution from the known constants of the molecule is presented and shown to be in semi-quantitative agreement with the facts in the case of the following band systems: SiN, AlO, CO (fourth positive group of carbon), I_2 (absorption), O_2 (Schumann-Runge system), CN (violet system), CO (first negative group of carbon), N_2 (second positive group of nitrogen), and N_2 (first negative group of nitrogen).

In the case of I_2 there is a discrepancy, if Loomis' assignment of n'' values is used, which does not appear if Mecke's original assignment is used. It is suggested that at least some of the lower levels postulated by Mecke are real but that absorption from them always results in dissociation of the molecule and so they are not represented in the quantized absorption spectrum.

1. Introduction

THE problem of the explanation of relative or absolute intensities of spectral lines stands out today as one of the most important in the whole field of spectroscopy. As yet the problem has hardly received the necessary attention from experimental workers to make attempts at quantitative theoretical treatment profitable. The experimental difficulties of constructing controllable sources of excited materials seem to be yielding but slowly to the tremendous efforts toward their removal which are now being made. However, as is known, considerable progress has already been made in the discussion of relative intensities in the fine structure of lines (notably hydrogen Balmer lines in the Stark effect) and more recently in the relative intensities in multiplets in line spectra and of the various lines in the fine structure of individual bands.[1]

When the fine structure of lines or bands is under discussion the experimental problem is considerably easier, for in this case the difficulties of the unknown variation of photographic sensitivity with wave-

* A preliminary account of this paper was presented at the meeting of the Pacific Coast Section of the American Physical Society at Stanford University in March, 1926.

[1] Sommerfeld, Atombau und Spektrallinien. 4th ed. Chap. 5.

length do not make themselves felt appreciably. But when relative intensities are desired over long stretches of the spectrum, as between the members of a series of lines in atomic spectra or as in a system of bands in molecular spectra, the difficulties of photometric work present themselves in their full force. The result is that today there are few quantitative data in this field. In the case of the individual bands of a system,—the special subject of this article,—one has only the rough visual estimates of the observers; sometimes nothing better than a knowledge of the presence or absence of the band in question under very roughly described conditions of excitation and observation.

It seems worth while, however, to undertake an attempt at a theoretical correlation of the outstanding characteristics of the observed data with the quantum theory model for the emitter of the band spectra of diatomic molecules. The theory presented here is one of the relative likelihood of the various possible changes in the vibrational quantum number and makes no attempt to explain the distribution of molecules in the initial state. The distribution in the initial state, in cases approaching thermal equilibrium, should be governed by the Maxwell-Boltzmann distribution law. This is apparently the case *within the accuracy of the known data* for absorption spectra, where deviations from thermal equilibrium are least important.[2] The Maxwell-Boltzmann law seems also to hold remarkably well in some cases of violent electrical excitation in discharge tubes where one hardly expects to find thermal equilibrium. Perhaps this is a reflection of the fact that the Maxwell-Boltzmann law is one of a sort of maximum chaos, and it matters not whether the chaos results from disordered heat motions or irregular electrical conditions. To be more concrete, if n' is the vibration quantum number of the excited electronic state of the molecule and n'' that of the normal state of the molecule, then the theory presented here undertakes the discussion of what Birge has called an n' progression for the emission process or an n'' progression for the absorption process.

One expects the considerations of which use is made in the model discussed to be of an approximate nature only. They are based on certain kinematic relationships existing between the vibratory motions in the two electronic states concerned. As the simple mode of discussing the model is one which, without quantum theory, would yield fractional changes in the vibrational quantum numbers, the question arises as to the proper modification of the results of the continuous theory in order

[2] Chapter IV, Sec. 4, of National Research Council Report on Molecular Spectra (in press). The writer is indebted to Professor R. T. Birge for the opportunity to use the manuscript copy of this report.

to fit the discontinuous quantum theory. There is as yet no known way of treating this problem so the present results are necessarily approximate.

In view of the fact that the latest development in the disentanglement of the quantum enigma is in the direction of the substitution of another kinematics[3] for the description of mechanical systems whose sizes are of the order of Angstrom units it is thought best not to dwell too long on the attempt to formulate this treatment exactly. Rather it is recorded here as giving results in striking and partially satisfactory agreement with the facts although with the expectation that a better treatment must come through the application of the newer kinematics of Heisenberg, Born, and Jordan.

The modern quantum theory interpretation of electronic bands as presented in Sommerfeld's "Atombau"[4] and in the National Research Council Report on Molecular Spectra (in press) is adopted in this paper. The quantization of the motion of a diatomic molecule leads to energy levels associated with each electronic configuration which are specified by a rotational and a vibrational quantum number, m and n respectively, as given by the following formulas:

$$\frac{E}{hc}=A_n=B_nm^2=D_nm^4=F_nm^6=\cdots$$

$$A_n=\omega^0n(1-\alpha n+\cdots)$$

$$B_n=B_0-\alpha n+\cdots$$

$$D_n=D_0+\cdots$$

All of the expressions are, in fact, infinite series but the terms indicated suffice for the analysis of most band systems. The derivatives of the potential energy curve at its equilibrium point are given in terms of the empirically determined, ω^0, x, B_0, α $\cdots$ by the formulas:[5]

$$V'(r_0)=0$$

$$V''(r_0)=c^2(2\pi\omega^0)^2\mu$$

$$V'''(r_0)=-\frac{6V''(r_0)\pi\sqrt{2B_0\mu c}}{\sqrt{h}}\left(\frac{\alpha\omega^0}{6B_0^2}+1\right)$$

$$V^{IV}(r_0)=\frac{2}{V''(r_0)}\left[\frac{5}{6}[V'''(r_0)]^2-8\frac{x}{ch\omega_0}[V''(r_0)]^3\right]$$

[3] Heisenberg, Zeits. f. Physik **33**, 879 (1925); Born and Jordan, Zeits. f. Physik **34**, 858 (1925); L. de Broglie, Ann. d. Physique **3**, 22 (1925); Schrödinger, Ann. der Physik **79** 459 (1926).

[4] Sommerfeld, Atombau, 4th ed., Chap. 9.

[5] The formulas are given by Born and Hückel, Phys. Zeits. **24**, 1 (1925). The nomenclature used here is that of the Report on Molecular Spectra.

in which c is the velocity of light and μ is the harmonic mean of the masses of the two atoms in the molecule.

2. General Theory for Abrupt Structural Changes

The theory of transition probability which will now be developed is an outgrowth of a picture proposed by Franck for a mechanism for the dissociation of molecules by absorption of light.[6] Briefly Franck's picture is as follows:

In a "cold" gas the molecules are not vibrating and are in their lowest electronic level so that the nuclear motions are governed by $V_1(r)$. If now a light quantum is absorbed which is of sufficient energy to bring the molecule into an electronic excited state, it is natural to suppose that in thus changing the electronic energy of the molecule no other specific action is exerted by the light on the molecule. The absorption of light merely substitutes a new law of nuclear interaction, say $V_2(r)$ for the old one $V_1(r)$. But since this new one has a different equilibrium position, the atoms, at the instant after the absorption, will be away from equilibrium and so start to vibrate. Should it happen that

$$V_2(r_{01}) > V_{2\max}$$

where $V_{2\ \max}$ is the maximum value of $V_2(r)$ in the range $r_{01} < r < \infty$ then the molecule will tend to execute oscillations of infinite amplitude, i.e., the molecule will dissociate. Thus Franck contemplates the photochemical dissociation of a molecule by a simple absorption of light.

It is natural to extend this point of view to the effect of an electron transition in a molecule either in absorption or emission and whether the molecule be vibrating in the initial state or not. The electron transition is supposed to happen in a negligibly short time as compared to the period of the nuclear vibrations. If the transition occurs at the instant when the separation of the atoms is r and the relative momentum is p_r then one supposes that the transition does not alter the instantaneous values of r and p_r but merely substitutes a new potential energy function, say $V_2(r)$, for the old one, say $V_1(r)$. The values of r and p_r at the instant of transition determine exactly a vibrational motion in the final state.

In general, of course, the vibrational motion so determined is not one of the states allowed by the quantum conditions. It becomes necessary, therefore, to suppose that the vibrational motion of the final state is not strictly governed by this principle but that it merely tends to take up the quantized vibration nearest to the one indicated by this principle.

[6] Franck, Trans. Faraday Society (1925).

Here a certain ambiguity appears which is akin to that which occurs in all other cases where attempts are made to reason accurately from properties of the orbits, other than their energies.

It is easy to give a general analytical formulation of the action governing the vibrational transition. Disregarding rotation and writing p for p_r, and q for r one has for the Hamiltonian functions of the initial and final states:

$$H_1=\frac{p^2}{2\mu}+V_1(q)$$

$$H_2=\frac{p^2}{2\mu}+V_2(q)$$

If the motion in either state is solved by the Hamilton-Jacobi method leading to the introduction of the action and angle variables, J_1w_1 for the initial state and J_2w_2 for the final state one finds relations of the form

$$p=p_1(J_1,w_1)$$
$$q=q_1(J_1,w_1)$$ for the initial state,

and similar relations for the final state. On the assumption underlying the work, if the electron transition takes place at an instant when the initial values of J and w are J_1,w_1 then the values of J and w after the transition, i.e., J_2 and w_2 will be given by the equations:

$$p_2(J_2,w_2)=p_1(J_1,w_1)$$
$$q_2(J_2,w_2)=q_1(J_1,w_1)$$

Or solving these equations for J_2 and w_2 one finds that:

$$J_2=J_2(J_1,w_1)$$
$$w_2=w_2(J_1,w_1)$$

so that the final motion is wholly determined by the initial motion. By the quantum conditions J_1 equals n_1h and J_2 equals n_2h where n_1 and n_2 are integers. It is thus seen that the solution for J_2 will not, in general, give an integral value. The phase of the final motion as given by w_2 plays no rôle in the spectroscopic theory. Moreover w_1 enters through a function which is periodic, with period 1 with respect to this variable. Thus the full range of possible values of J_2 corresponding to any J_1 is obtained by letting w_1 range from 0 to 1. From the general dynamical theory w_1 increases linearly with the time. Failing any other indications on this point, one may say that the electron transition is just as likely

to occur at one instant as at another, and thus there is a definite probability assigned to each range of J_2 to J_2+dJ_2.

It is clear that if all values of w_1 are equally probable then the values of J_2 corresponding to the small values of dJ_2/dw_1 will be strongly weighted. But $dJ_2/dw_1=0$ give the maxima and minima of the possible transitions so that these extremes are to be regarded as more probable than the other allowed jumps.

But the uncertainty of how to treat the fractional n_2 and the inaccuracy of the experimental data make it fruitless to attempt to consider such detailed questions as the accurate relative probabilities of the transitions. For a given J_1 there will be a maximum and minimum value of J_2 given by the theory. Moreover the most probable transitions, it will appear later, are to the extremes of J_2 if the times of electron transition be taken as equally probable. Therefore in discussing the relationship of the theory to empirical facts, only the extremes of J_2 for each J_1 have been computed.

Looking over the theory as just developed, it is to be emphasized that at least the extrema of J_2 for each J_1 are governed entirely by the energy functions $V_1(r)$ and $V_2(r)$. These in turn, as has been pointed out, are fixed by the positions of the bands in the spectrum. Thus there are no adjustable constants appearing in the theory so that *the vibrational transition probabilities are sharply correlated with the structure of the band system as regards position in the spectrum.*

The actual solution of the equations which present themselves in the case of the non-harmonic oscillator is prohibitively lengthy. In the following section the explicit formulas are developed for the case in which all derivatives of $V_2(r)$ and $V_1(r)$, higher than the second, vanish (harmonic oscillator). A graphical mode of treating the non-harmonic case is also presented.

3. Explicit Formulas for the Harmonic Oscillator

In the case in which $V_1(r)$ and $V_2(r)$ are parabolic the modes of vibration are simple harmonic in both initial and final states and the explicit development of the formulas is quite simple. Thus let us assume:

$$V_1(q)=\tfrac{1}{2}K_1(q-q_{01})^2$$
$$V_2(q)=\tfrac{1}{2}K_2(q-q_{02})^2$$

The solution for p and q in terms of J and w for the harmonic oscillator is well-known.[7] One has for the final state:

[7] Born, Vorlesungen über Atommechanik, pp. 39, 57.

$$p_2(J_2, w_2) = \sqrt{2\mu\nu_2 J_2}\cos 2\pi w_2$$

$$q_2(J_2, w_2) = q_{02} + \frac{1}{2\pi}\sqrt{\frac{2J_2}{\mu\nu_2}}\sin 2\pi w_2$$

in which the frequency ν_2 is related to the mass μ and the spring constant K_2 by

$$\nu_2 = \frac{1}{2\pi}\sqrt{\frac{K_2}{\mu}}$$

Similarly for the initial state:

$$p_1(J_1 w_1) = \sqrt{2\mu\nu_1 J_1}\cos 2\pi w_1$$

$$q_1(J_1 w_1) = q_{01} + \frac{1}{2\pi}\sqrt{\frac{2J_1}{\mu\nu_1}}\sin 2\pi w_1$$

Equating the values of p and q at the instant of the electron transition and writing d for $q_{01} - q_{02}$:

$$\sqrt{2\mu\nu_2 J_2}\cos 2\pi w_2 = \sqrt{2\mu\nu_1 J_1}\cos 2\pi w_1$$

$$\frac{1}{2\pi}\sqrt{\frac{2J_2}{\mu\nu_2}}\sin 2\pi w_2 = d + \frac{1}{2\pi}\sqrt{\frac{2J_1}{\mu\nu_1}}\sin 2\pi w_1$$

Solving for J_2 in terms of J_1 and w_1 by elimination of w_2:

$$J_2 = 2\pi^2\mu\nu_2 d^2 + \frac{1}{2}\left(\frac{\nu_1}{\nu_2} + \frac{\nu_2}{\nu_1}\right)J_1 + 2d\sqrt{2\pi^2\mu\nu_2\frac{\nu_2}{\nu_1}}\sin 2\pi w_1 \cdot \sqrt{J_1}$$
$$+ \frac{1}{2}\left(\frac{\nu_1}{\nu_2} - \frac{\nu_2}{\nu_1}\right)\cos 4\pi w_1 \cdot J_1$$

The solution for w_2 in terms of J_1 and w_1 is readily obtained but it is not needed. Introducing the quantum integers n_1 and n_2 in place of J_1 and J_2:

$$n_2 = \frac{2\pi^2\mu\nu_2}{h}d^2 + \frac{1}{2}\left(\frac{\nu_1}{\nu_2} + \frac{\nu_2}{\nu_1}\right)n_1 + 2d\sqrt{\frac{2\pi^2\mu\nu_2}{h}\cdot\frac{\nu_2}{\nu_1}}\sin 2\pi w_1 \cdot \sqrt{n_1}$$
$$+ \frac{1}{2}\left(\frac{\nu_1}{\nu_2} - \frac{\nu_2}{\nu_1}\right)\cos 4\pi w_1 \cdot n_1$$

For brevity this will be written:

$$n_2 = A + Bn_1 + C\sqrt{n_1}\sin\theta + Dn_1\cos 2\theta,$$

defining the coefficients A, B, C, D by comparison with the preceding

equation. The extreme values of n_1 corresponding to any n_2 are found by the roots of $dn_1/d\theta=0$ in the usual way. If $C/4D\sqrt{n_1}|>1$

$$n_2=A+Bn_1\pm C\sqrt{n_1}\mp Dn_1$$

and if $|C/4D\sqrt{n_1}|<1$ in addition to these also secondary maxima, given by $n_2=(A-C^2/8D)\pm C^2/4D+(B+D)n_1$ the $\pm$ sign being taken the same as the sign of $C/4D$.

As has already been remarked, the extreme allowed transitions are the most probable ones and therefore these equations for the extrema give the bands which one expects to be strongest in a band system.

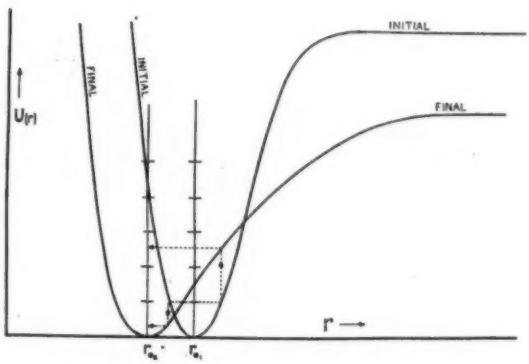

Fig. 1. Typical relation of the potential energy curves, illustrating graphical method of finding favored transitions.

The formulas for the non-harmonic oscillator can be obtained by successive approximations in a purely analytical way but it is easier to resort to an approximate graphical method. $V_1(r)$ and $V_2(r)$ are supposed to have been determined, in the neighborhood of r_{01} and r_{02} respectively from the analysis of the energy levels of the band system. Suppose these plotted on the same piece of paper. Also suppose the vibrational energy levels marked off as in Fig. 1. Then when the molecule vibrates in either electronic state with a known number of quanta it is easy to see what the amplitude of the motion is, for from the energy integral, $p=0$ when

$$V(r)=W$$

if W is the energy of the vibratory motion. It is at the two extreme positions that the vibrator spends most of the time, i.e., the electronic transition is most likely to occur when the vibrator is in one of these

extreme positions. At these extreme values of r for a vibratory motion given by $V_2(r)$, if $V_1(r)$ is suddenly made the law governing the motion then one sees directly from the figure what will be the amplitude and hence the energy of the new motion. Thus two most probable transitions are determined for each value of the quantum number in the initial state.

This graphical method, as will appear later, indicates how very sensitive the theory is to slight uncertainties in the functions, $V(r)$. In the next section are given the details of the application of the theory to all systems for which the necessary data are available.

4. Application to Known Systems

It will now be seen how far the model employed accounts for the main observed features of intensity distribution in band systems. These have

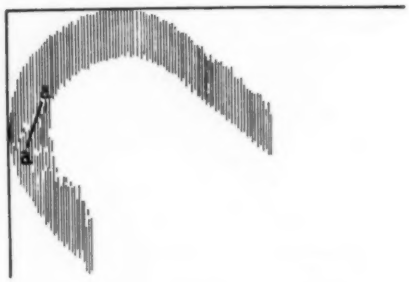

Fig. 2. Typical distribution of intensity in band system (n' ordinates, downward; n'', abscissas).

been discussed by Birge[8] who points out that it is a general rule that for each value of n' (the quantum number of the initial state for emission) there are two preferred values of $n'-n''$. On a double entry table as normally used, the n' being plotted downward as ordinates and the n'' to the left as abscissas the locus of the strong bands is a parabolic looking curve; i.e., the strong bands form a locus somewhat like the shaded part in Fig. 2. The size of this general locus with regard to the coordinate scale varies greatly from system to system, the branches being coincident for SiN, slightly separated for AlO, widely separated for CO while the scale for iodine is so great that only the part near the origin (a in the figure) is known. In this section the connection between these observed distributions and the theoretical predictions will be examined.

[8] Birge, Phys. Rev. **25**, 240 (1925), Abstract No. 23, also Chap. IV, Sec. 4, Report on molecular spectra.

The band systems to be treated are in order, SiN, silicon nitride; AlO, aluminum oxide; CO, 4th positive group of carbon; I_2, iodine; also O_2, Schumann-Runge system, CN, violet cyanogen; CO^+, first negative group of carbon, N_2, second positive group of nitrogen and N_2^+, first negative group of nitrogen. Of these nine systems, the first four are typical of the increasing scale of the intensity distribution and are discussed in greater detail. In CO and I_2 the deviations from the harmonic law of force are considerable. For these cases corrections for the deviations are discussed as fully as the data allow. For the remaining five systems the observed intensity data together with the theoretical curve calculated from an assumption of harmonic force law are presented as additional examples of the semi-quantitative correctness of the theory.

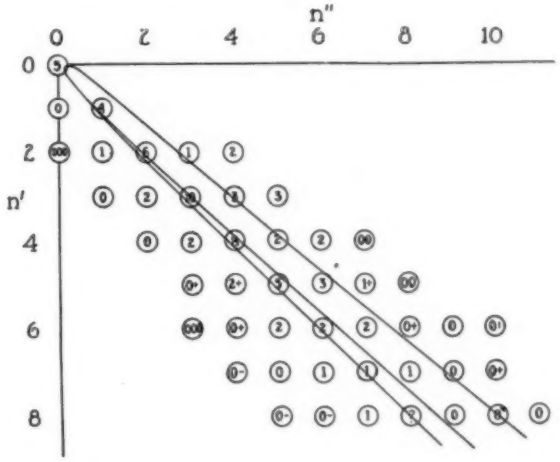

Fig. 3. The band system of silicon nitride.

In Table I are collected together all of the molecular constants which are needed for a discussion of the systems according to the harmonic force law. In every case the figures are taken from a large table of constants in Chapter IV of the National Research Council Report on Molecular Spectra. In the last four columns of the table are given the four constants A, B, C, D which occur in the formula for n'' in terms of n' as computed for the emission process. C.G.S. units are employed. A quantity with $'$ refers to the initial state and $''$ to the final state of the emission process. $\omega^{0\prime}$ is the ν_1 of the previous section expressed in cm^{-1} instead of sec^{-1}, similarly for $\omega^{0\prime\prime}$ and ν_2.

Turning now to the first system, one has available the estimated intensities by Mulliken.[9] These are plotted in Fig. 3. Here there is but a

[9] Mulliken, Phys. Rev. **26**, 319 (1925); Jevons, Proc. Roy. Soc. **89A**, 187 (1913–14).

TABLE I.—*Summary of molecular constants*

Carrier	$\mu \times 10^{24}$	ν_0^* cm^{-1}	ω' cm^{-1}	ω'' cm^{-1}	$I_0' \times 10^{40}$	$I_0'' \times 10^{40}$	$r_0' \times 10^8$	$r_0'' \times 10^8$	$d \times 10^8$	A	B	C	D	$(C/4D)^2$
SiN	15.417	24234.2	1016.3	1145.0	37.8	37.2	1.567	1.554	+0.013	0.0269	1.007	+ 0.349	−0.119	0.537
AlO	16.60	20635.3	864.8	970.	46.01	43.38	1.665	1.617	+0.048	0.335	1.007	+ + 1.23	−0.115	7.1
CO	11.317	64721.	1499.28	2147.74	17.3	14.9	1.24	1.17	+0.07	1.075	1.065	+ + 2.485	−0.366	2.88
I_2	104.7	15598.3	126.52	213.76	1210.	787.	3.40	2.74	+0.66	88.0	1.140	+24.4	−0.548	124.
					1115.	720.5	3.622	2.622	+0.640	82.8		+ 23.62		
O_2	13.17	49359.3	708.	1565.	34.22	19.2	1.61	1.21	+0.40	29.8	1.331	+ 16.24	−0.879	21.4
CN	10.67	25799.8	2143.9	2055.64	14.140	14.647	1.151	1.172	−0.021	0.875	1.001	+ − 1.833	+0.043	113.
CO^+	11.317	45637.7	1704.42	2197.03	15.4	14.05	1.17	1.11	+0.06	0.809	1.033	+ + 2.045	−0.256	3.98
N_2	11.558	29653.1	2018.66	1718.40	15.24	16.98	1.149	1.212	−0.063	0.712	1.013	+ − 1.56	+0.161	5.87
N_2^+	11.558	25565.9	2396.0	2187.4	13.35	14.41	1.075	1.117	−0.042	0.403	1.004	+ − 1.213	+0.092	10.9

*ν_0 gives the frequency of the origin of the 0-0 band.

single ridge of strong bands. The figure shows the curve of most probable values of n'' as a function of n', calculated from the molecular constants according to the theory. As the theoretically double-branched curve is here scarcely an integer in width, it is natural that the double branch should have merged into one for the rough correspondence in question. This molecule is one which shows a doubling of the lower branch due to the cos 2θ term in the formula. The strong bands coincide exactly with this doubled line.

The next typical case is that of aluminum oxide. Here the experimental data both of Birge and also of Eriksson and Hulthén show clearly the double ridge of strong bands.[10] Here the curve computed from the molecular constants for the locus of the strong bands is open enough so that the branches should appear distinct, as in fact they are. The lower branch of the theoretical curve agrees precisely with the data, while the upper branch is slightly high. This distribution of intensity is by far the most common in the systems of bands which have thus far been analyzed on the quantum theory, as can be seen in Table I from inspection of the table of values of A, B, C, and D.

Extending the sequence of increasing scale for the distribution curve, the next example is the great system of the fourth positive group of carbon which is now known to be due to carbon mo-

[10] Birge has made estimates from unpublished spectrograms taken by him at the University of Wisconsin. Also Eriksson and Hulthén, Zeits. f. Physik **34**, 775 (1925).

noxide.[11] In this one system, which extends from about 2650A to 1300A there are known more than 150 different bands. The great extent of this system over the frequency scale (40,000 cm^{-1}) naturally furnishes a severe test of any intensity theory. Unfortunately there are here no even semi-quantitative intensity data. In fact no one observer has ever photographed the entire system. Because of its great extent, however, the main features of the distribution are indicated by a diagram which shows simply which bands are observed. This accordingly has been done in Fig. 6. The full line gives the curve of the intensity distribution as computed by the simple theory based on the harmonic law of force.

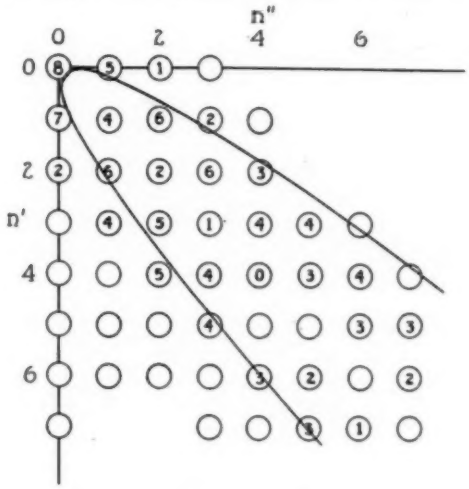

Fig. 4. The band system of AlO.

The analysis of the fine structure of the bands is so incomplete that it is only possible in a rough way to find the corrections due to deviations from the harmonic force law. In fact no fine structure work has been carried out on this system. Data on the initial state may be obtained since this, according to the analysis of Birge, is also the final state of the Angstrom CO bands. The moment of inertia in the final state is obtained from the infra-red CO rotation vibration bands. Besides the data given in Table I, the following figures on the 4th positive group are used in this work:

$$x'\omega^{0'} = 17.24 \qquad \alpha' = 0.023$$
$$x''\omega^{0''} = 12.703 \qquad \alpha'' = ?$$

By means of the formulas for the coefficients in the law of force already given, it is possible from these data to compute force law curves for both

[11] Birge, Nature **117**, 229 (1926); Lowry, J.O.S.A. **8**, 647 (1924).

states, but with some ambiguity and considerable uncertainty in the final state, for which no α value is known. Writing the expansion for the potential energy in the form

$$V = u_2(r-r_0)^2 + u_3(r-r_0)^3 + u_4(r-r_0)^4 + \cdots$$

in which the unit of energy is spectroscopic wave numbers (cm^{-1}) while $(r-r_0)$ is expressed in Angstrom units one readily finds from the formulas previously given the following expressions for u_2 u_3 and u_4 in terms of the band structure constants:

$$u_2 = \frac{10^{-16}V''(r_0)}{2!hc} = [0.95641-3](\omega^{0^2}\mu)$$

$$u_3 = \frac{10^{-24}V'''(r_0)}{3!hc} = -[0.27924-1]u_2\sqrt{B_0\mu}\left(\frac{\alpha\omega^0}{6B_0^2}+1\right)$$

$$u_4 = \frac{10^{-32}V^{IV}(r_0)}{4!hc} = \frac{1}{u_2}\left(\frac{5}{4}u_3^2 - \frac{8}{3}u_2^3\frac{x}{\omega^0}\right)$$

In these expressions the unit of μ is 10^{-24} gm as in Table I, and the quantities in brackets are the logarithms of the coefficients of the corresponding quantities.

When the formulas are applied to the known data for the initial state in CO one obtains the following values:

$$u_2' = 2.30\times10^5$$
$$u_3' = -6.00 \text{ "}$$
$$u_4' = +8.84 \text{ "}$$

For the final state a value of α is lacking. In computing the potential energy curve what seems like a reasonable value of α has been used, namely 0.02. This compares well with the known values for systems which have been analyzed. The coefficients found on this assumption are:

$$u_2'' = 4.718\times10^5$$
$$u_3'' = -12.59 \text{ "}$$
$$u_4'' = +25.66 \text{ "}$$

In Fig. 5 are drawn to scale the potential energy curves of the initial and final states in a form suitable for the application of the graphical method of predicting the intensity distribution. In Fig. 6 is given in the curve marked "corrected law" the theoretical position of the two ridges of intense bands as obtained by this method. It is clear that the corrected law improves the agreement for the lower branch while leaving almost unaltered the good fit of the other branch.

Passing now to the band system of iodine,[12] the largest known band system, it is essential to use the higher terms in the law of force since the change in the moment of inertia between the initial and the final states is very large.

The calculations make use of the following data in addition to that given in the table:

$\alpha' = 0.00015$ $\qquad x'\omega^{01'} = 0.85$

$\alpha'' = 0.00011$ $\qquad x''\omega'^{011'} = 0.592$

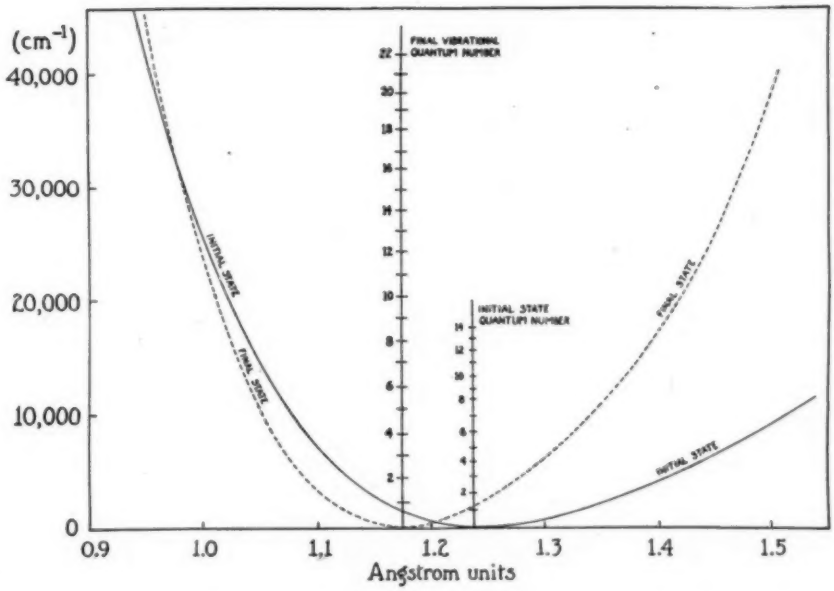

Fig. 5. The potential energy curves for the two electronic states involved in the fourth positive group of carbon (CO).

The resulting values of the coefficients in the potential energy function are:

	Initial	*Final*
u_2:	$+1.537\times10^4$	$+4.313\times10^4$
u_3:	-2.906 "	-6.002 "
u_4:	$+3.580$ "	$+4.014$ "

[12] The analysis is due to Mecke, Ann. d. Physik **71**, 104 (1923), with Loomis' revision of the quantum assignment. The values of B_0'' and α are due to Loomis (Chapter VI, Report on Molecular Spectra), that of α'', however, having been previously given by Kratzer and Sudholt, Zeits. f. Physik **33**, 144 (1925). As Loomis points out, the values of α are quite uncertain. For new observations on resonance spectra, see Dymond, Zeits. f. Physik, **34**, 553 (1925).

As in the case of CO, there are no intensity measurements available for this system of bands. The data are due to Mecke and give merely the presence or absence of the various bands. The system is thus plotted in Fig. 7. Here the data are for the *absorption* spectrum rather than for emission as in the examples previously given. To be consistent with the other examples, however, the terms "initial" and "final" in the foregoing set of constants have been chosen so as to refer to the *emission* process. In the absorption process, n'' becomes the initial quantum number and n' the final. Mecke has already commented on the peculiar intensity distribution in I_2, his Fig. 4 contrasting it with the more typical dis-

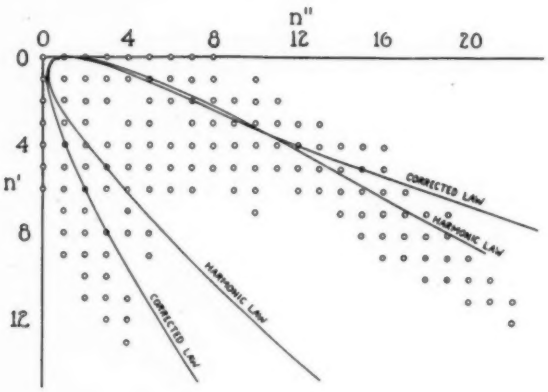

Fig. 6. The observed bands of the fourth positive group of carbon.

tribution of intensity of the violet CN-system. The distribution of intensity is, of course, profoundly modified by the distribution of the molecules among the initial states. This accounts for the great observed decrease in intensity of successive n' progressions, for increasing values of n''.

The curve in Fig. 7 is that which is obtained by the graphical process, using the potential energy curves given by the foregoing set of constants. Here evidently is a wide discrepancy between theory and experiment. The discrepancy may be removed by an alteration in the assignment of vibrational quantum numbers. Mecke's assignment of values of n'' is greater by four than the one, due to Loomis, on which the calculations have been based. Mecke's zero of n'' was chosen to include a place for four anti-Stokes terms in Wood's resonance spectrum. But if the theoretical intensity curve derived from Loomis' assignment is correct it is clear that a molecule in the zero-state initially would favor a transition to an energy state in excess of that required for the dissociation process.

This suggests that when the molecule absorbs light from the unexcited non-vibrating state it is always dissociated and no bands are obtained. It is therefore possible that lower vibrational states exist which contribute, by absorption from them, only to the continuous spectrum of iodine. The existence of such lower states is called for, of course, if there are really the so-called anti-Stokes terms in the resonance spectrum of Iodine. Loomis has, however, given an analysis of the resonance doublets which makes it appear that what were believed to be anti-Stokes terms in the $n'=26$ progression are really due to the excitation of some lines out of other n' progressions. Dymond has recorded observations of

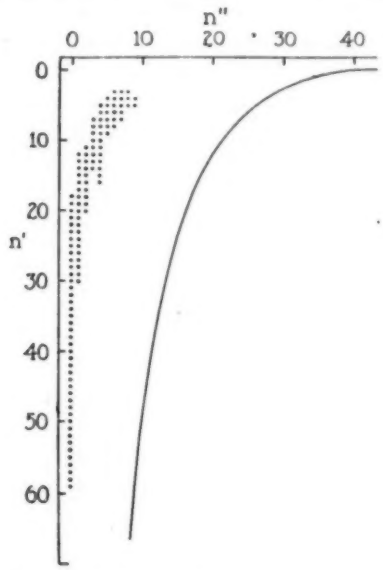

Fig. 7. The absorption bands of iodine (I_2).

anti-Stokes terms in resonance spectra excited by other lines than the green mercury line. It remains to be seen whether Loomis' analysis can be applied to them. It is clear that, since the theory here presented gives the same favored Δn values for absorption as for emission, transitions involving the lower levels in the unexcited state would not appear in the fluorescent spectrum for the same reason that they are not involved in the fully quantized absorption spectrum. Thus it is to be expected that anti-Stokes terms will not appear even though the necessary levels may exist in the molecule.

It is easy to see that a rather small change in the assignment of quantum numbers will make the theory agree with experiment. Full calculations were carried out for the case in which the n'' values were increased

by 5 and the n' by 30. It was found that the discrepancy was about the same but in the other direction. Therefore a good fit could be obtained by some reassignment which makes smaller changes in n' and n''. It seems, however, that agreement on the intensities calls for reassignment of *both* n' and n'', since calculations show that good fits are not obtained if n' alone is altered. Iodine, then, may be tentatively regarded as in agreement with the theory.*

This completes the consideration of the four main sizes of the typical intensity distribution. Of the remaining five, the Schumann-Runge system of oxygen is much like that of iodine in that an unusually large change in the moment of inertia occurs during the electron transition. The other four are medium sized systems like that of AlO.

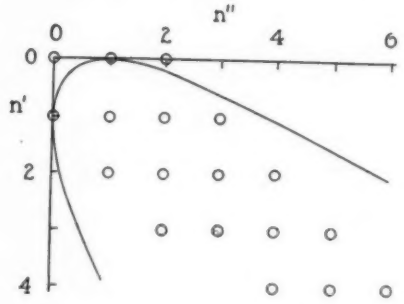

Fig. 8. The violet cyanogen system (CN).

The Schumann-Runge bands of oxygen are quite incompletely known.[13] This name is here given to the system whose $n''=0$ progression is known in absorption by the researches of Schumann and others and whose $n'=0$ progression was photographed in emission by Runge. The recognition of the fact that the Runge and Schumann bands are part of one system is due to Mulliken. The data on the absorption bands has recently been extended by the work of Leifson as interpreted by Birge. All that can be said here is that in absorption Leifson's strongest bands run from $n'=9$ to a limit at $n'=21$ with continuous spectrum beyond. Similarly the emission bands measured by Runge correspond to large values of Δn, the actual bands being $n'=0$, $n''=11$ to 17. Here is evidently a preference for large values of Δn which is quite in accord with the theory of this paper. The fine structure analysis of the bands thus

[13] Schumann, Smithsonian Contrib. **29**, no. 1413 (1903); Runge, Physica **1**, 254 (1921); Mulliken, Private communication to Professor Birge; Leifson, Astrophys. J. **63**, 73 (1926); Füchtbauer and Holm, Phys. Zeits. **26**, 345 (1925); Report on Molecular Spectra, Chap. IV, Section 7.

* See note on p. 1201.

far permits only the use of parabolic $V(r)$ curves, but these, when computed from the data of Table I show that in absorption the most probable transition is that beyond dissociation. The calculation shows that from the $n''=0$ state the molecule in the absorption process tends to take up over 1.2 volts of vibrational energy or 0.4 volts in excess of that needed for dissociation in the excited state for these bands. Similarly the curves indicate for the $n'=0$ progression of emission bands a large Δn, much larger in fact than that indicated directly by the Runge bands. Here the higher terms in the force law will undoubtedly operate to reduce the theoretical Δn, so that in this system there is as good agreement as can be hoped for in the present state of analysis of the bands.

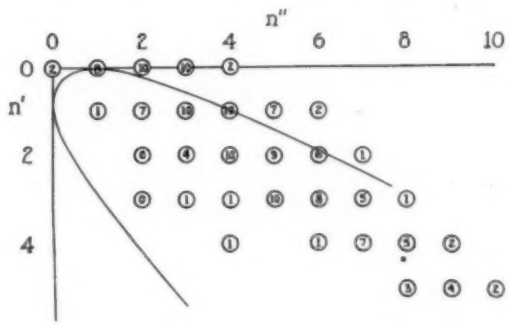

Fig. 9. The first negative group of carbon (CO^+).

The remaining four band systems to be considered present no new features of special interest. They are shown in Figs. 8, 9, 10, 11 in which the intensities are, when given, simply rough visual estimates from the plates. The theoretical curve in each case is based on the formula which assumes simple harmonic oscillators. The data for CN (Fig. 8), are from Heurlinger.[14]

The intensities given for CO^+ (Fig. 9) as well as the molecular constants used are based on the work of Blackburn and Johnson.[15] It is important to note that the theory predicts the existence of some strong emission bands in the far ultraviolet, along the lower branch of the theoretical curve. The single-branched intensity distribution the writer believes is entirely a consequence of the lack of complete experimental data. The intensity estimates for the second positive group of nitrogen (Fig. 10) are due to Birge, being made from inspection of spectrograms taken by E. P. Lewis.[8]

[14] Kayser's Handbuch, v. 5, p. 190.

[15] Johnson, Proc. Roy. Soc. **108A,** 343 (1925); Blackburn, Proc. Nat. Acad. **11,** 28 (1925).

The data on the first negative group of nitrogen (Fig. 11) are due to Merton and Pilley.[16]

In conclusion it seems permissible to claim that the theory outlined here gives a satisfactory semi-quantitative correlation between the

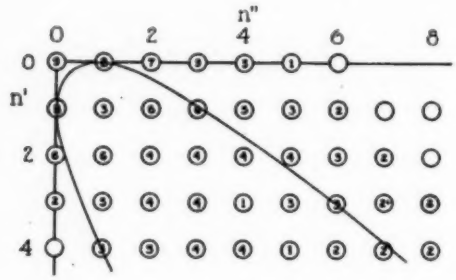

Fig. 10. The second positive group of nitrogen (N_2).

intensity distribution in band systems and the positional structure of the systems by means of a definite mechanical picture of the processes governing transition probabilities. The only previous attempt at a theoretical treatment of this topic is that of Lenz[17] who gave, by application of the correspondence principle to an over-simplified molecular

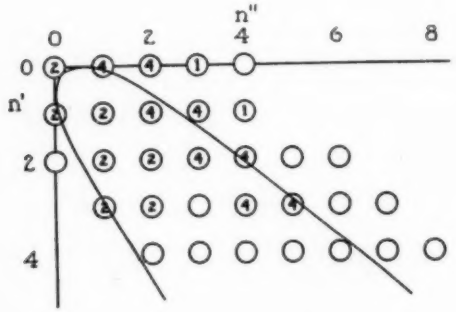

Fig. 11. The first negative group of nitrogen (N_2^+).

model, some general formulas which, however, were incapable of numerical application to specific cases. On the other hand, Lenz' theory does lead to an understanding of the many and seemingly irregular alternations of intensity in the $n' = 26$ progression of the iodine emission spec-

[16] Merton and Pilley, Phil. Mag. **50**, 195 (1925).
[17] Lenz, Zeits. f. Phys. **25**, 299 (1924).

trum (Wood's resonance spectrum). This is a thing which is wholly unclear in terms of the theory given here.

It is a pleasure to acknowledge my indebtedness to Professor R. T. Birge who has generously given me the benefit of his knowledge of band spectra and their quantum interpretation. It is also appropriate again to call attention to the fact that my work is merely an extension of a leading thought on this subject by Professor J. Franck.

UNIVERSITY OF CALIFORNIA,
DEPARTMENT OF PHYSICS,
July 27, 1926.

Note added to proof.—Since this was written I have learned of the experiments of H. Kuhn (Zeits. f. Physik **39**, 77 (1926)) which seem to show conclusively that the long series of absorption bands which have a convergence limit really do come from the lowest vibration level so that the values of n'' cannot be altered as suggested on page 1198.

GÖTTINGEN,
November 8, 1926.

ELECTRONIC STATES AND BAND-SPECTRUM STRUCTURE IN DIATOMIC MOLECULES
II. SPECTRA INVOLVING TERMS ESSENTIALLY OF THE FORM $B(j^2-\sigma^2)$

By Robert S. Mulliken

Abstract

Properties of rotational terms of the form $B(j^2-\sigma^2)$.—Evidence is presented to show that the AlH, He_2, and certain other bands involve rotational terms essentially of the form $B(j^2-\sigma^2)$, and are in agreement with the postulates of a previous paper.[1] Since terms of this form have not hitherto been recognized *in practice*, their chief empirical properties, as shown by the bands discussed below, are now summarized. (1) There are in general two values of the rotational energy term $F(j)$ for each j value. This type of rotational doubling has previously been confused with that which occurs, due to $\pm\epsilon$ (where $\epsilon=|\rho|$), when $F(j)$ is essentially of the form $B(j-\rho)^2$. In the special case where ρ and σ are both zero (^1S states), all rotational doubling is absent. (2) The two sets of $F(j)$ values, in doubling of the σ type, in general differ in respect to the values of B and of a small "secondary" ρ whose presence must, at least formally, be admitted; thus $F_i(j)=B_i[(j-\rho_i)^2-\sigma^2]+\cdots$ ($i=A$ or B), with $\epsilon<\frac{1}{2}$, or usually $\ll\frac{1}{2}$, in practice; a slight difference in the electronic term values may also occur (as e.g., in the He_2 bands). (3) In general, there are six branches in combinations of two σ-type terms (cf. Eqs. (2) of text); in the P and R branches, combinations occur only between like rotational terms ($F'_A\rightarrow F''_A$, and $F'_B\rightarrow F''_B$), while in the Q branches, "crossing over" always occurs ($F'_A\rightarrow F''_B$ or $F'_B\rightarrow F''_A$). (4) In the special case of $^1P-{}^1S$ and $^1S-{}^1P$ combinations (cf. Eqs. (1) and Fig. 1 of text), there are only three branches, due to the existence for the ^1S electronic state of only one rotational state for each value of j (these states have the properties of F_B states); apparent "combination defects" in P-Q-R combinations result here from the Q crossing over phenomenon. (5) In $^2S-{}^2P$ and $^2P-{}^2S$ transitions, the intercombination of the ρ-type ^2S term with the σ-type $^2P_1$ or $^2P_2$ term gives rise to a special band structure (with six branches) in which for a frequent limiting case there is a practically complete coalescence of one of the P with one of the Q branches, and of one of the R branches with the other Q branch (cf. Eqs. (8), (8A), and (8B) of text). The existence of these band-types is strong evidence for the reality of the ρ values $+\frac{1}{2}$ and $-\frac{1}{2}$ for ^2S states, and so affords additional confirmation of Kratzer's interpretation of the violet CN bands ($^2S-{}^2S$ transition) as adopted in ref. 1.

The CO, AlH, and He_2 bands.—Assuming $\rho=0$, $\sigma=1$ for ^1P states, it was shown in ref. 1 that the structure and missing lines of the CO Ångstrom bands are in agreement with the classification $^1P-{}^1S$ given by Birge. The AlH bands are now shown to fall under the classification $^1S-{}^1P$, and it is predicted that the fourth positive CO bands, designated as $^1S-{}^1P$ by Birge, will have the corresponding structure and missing lines.—By adopting the assumption (due to Mecke) that alternate lines are missing in each branch, it is shown

[1] R. S. Mulliken, Phys. Rev. **28**, 481 (1926).

that the three-branch "series" bands of helium are of the $^1S-{}^1P$ type and the three-branch bands λ6400 and 4546 of the $^1P-{}^1S$ type, while the six-branch band λ5733 appears as the (only known) representative of the $^1P-{}^1D$ type. Revised values of various constants of the He_2 molecule in its different electronic states are given in Table I. To account for the alternate missing lines, a system of alternate suppressed rotational levels (cf. Fig. 2) is assumed. The correctness of this system is supported by several lines of evidence in addition to the satisfactory interpretation of the band structures; e.g., it correctly predicts the absence of $^1S-{}^1S$ and $^1P-{}^1P$ transitions in He_2. The relation of the excited states of He_2 to those of He is discussed briefly.

Resonance series and the band spectra of the alkalies and the halogens. The fluorescent radiation emitted by a molecule after excitation by absorption of monochromatic light consists under suitable conditions of a series ("resonance series" of Wood) of roughly equidistant groups of band lines, corresponding to a series of final vibrational states. According to the present analysis, various transitions in even molecules should yield resonance series of the following types: $^1S-{}^1S$, *P-R* doublets; $^1P-{}^1P$ (or $^1D-{}^1D$, etc.), *P-Q-R* triplets but with the *Q* member usually too weak to be noticed; $^1P-{}^1D$, $^1D-{}^1P$, $^1P-{}^1S$, etc., *P-Q-R* triplets; $^1S-{}^1P$, doublet series (*P*,*R*) for some exciting wave-lengths and singlet series (*Q* only) for others. The visible I_2 absorption bands give rise to *P-R* doublets (interpreted as such by Lenz), so that they (and by analogy the corresponding Br_2 and Cl_2 bands) are probably $^1S-{}^1S$ (or perhaps $^1P-{}^1P$ or $^1D-{}^1D$). The Na_2 absorption bands in the green, giving both singlet and doublet resonance series, are probably $^1S-{}^1P$, and the same is probably true by analogy of most of the familiar alkali metal bands. In further support of this, there is no evidence, in the band structure, of electronic doublets such as appear in the atomic transitions $^2S-{}^2P_{1,2}$. The relation of the electronic states of Na_2 to those of Na is briefly discussed.

Other band spectra.—Although no detailed analyses are available, the evidence indicates that the red CN, BOα, and CO^+ comet tail bands (also the doublet alkaline earth halide bands?) have a structure (cf. (5) under "Properties . . . . ," above) essentially the same as that of the ZnH, CdH, and HgH bands, and characteristic of the transition $^2S-{}^2P_{1,2}$. The "combination" bands of BO and CO^+ and the NO third positive bands (presumably also Jevons' SnCl bands) probably have a similar structure characteristic of $^2P_{1,2}-{}^2S$ transitions. Predictions are given for the structure of $^2P-{}^2D$ bands; these should differ from all bands now on record in having T' and T'' both integral.—The OH, CH and MgH bands are briefly discussed following Table II, which gives a condensed summary of T, ρ and σ values, and electronic transitions, for the band types discussed here and in ref. 1. Table II shows that *in all known cases, j_e appears essentially as σ in P and D states, but as $\pm\epsilon$ in S states* (for ^1S states $j_e=0$). A corollary is that m is half-integral in known S states, but not in P or D states.

INTRODUCTION

IN previous papers certain examples of band spectra involving rotational energy terms essentially of the form $B(j^2-\sigma^2)$ have been discussed (CO Ångström bands,[1] ZnH, CdH, and HgH bands)[2]. In section *A* of the present paper, the structures of a number of further

[2] R. S. Mulliken, Proc. Nat. Acad. Sci. **12**, 151 (1926).

examples, involving singlet electronic states and due to even molecules, are interpreted; while in section *B* additional examples due to odd molecules and involving doublet electronic states are treated; in section *C* the interpretations of this and preceding papers are summarized.

Frequent reference will be made below to the first paper of this series[1] for notation, definitions, etc.; this paper will always be referred to as I. The system of j values used in the present paper is that adopted in I (cf. postulate *III*). As remarked in the "note added in proof" at the end of I, it is however likely that the true j values are all $\frac{1}{2}$ unit lower than those here used.

A. Spectra of Molecules with an Even Number of Electrons

General Relations. From I, the following relations are always to be expected for combinations of terms of the form $B(j^2-\sigma^2)$, in even molecules: (*1*) $j_e=\sigma=0$ for ^1S states, 1 for ^1P states, 2 for ^1D states, etc. (cf. postulate *I* of I); (*2*) j=half-integral (cf. postulate *III* of I); (*3*) $j\sim T$, since $T=j-\rho$ by definition (cf. I, p. 491) and since we are assuming $\rho\sim 0$; (*4*) hence $j\sim T\sim\sigma+\frac{1}{2}, \sigma+1\frac{1}{2}, \sigma+2\frac{1}{2}, \cdots$, (cf. I, p. 488, section on missing lines); (*5*) *P*, *Q*, and *R* branches are respectively *P*-, *Q*-, and *R*-form, since $\Delta T\sim\Delta j$ (cf. I, Eq. 5 and p. 492); (*6*) as a result of the presence of a σ (either σ' or σ'' or both,—cf. I, p. 488), *Q* branches should always be present (in addition to *P* and *R* branches) except for the special case of $^1S-{}^1S$ transitions ($\sigma'=\sigma''=0$). To avoid possible misunderstanding, it should be remarked that the exact values of σ' and σ'' have not been obtained from direct experimental evidence, but have been deduced from the missing lines, in connection with the postulates of I, as explained in I (cf. pp. 493-4).

In addition to these outstanding relations, there are a number of secondary but nevertheless important features which will now be stated in the form of probable empirical generalizations[3] in order to facilitate the discussion of individual spectra. The truth of these generalizations will at first be assumed, but will become increasingly evident as successive examples are considered.

Empirically, there are two rotational states for each value of j when $\sigma>0$ (^1P, ^1D, $\cdots$ states), but only one when $\sigma=0$. This rotational doubling superficially resembles that for terms of the type $B(j-\rho)^2$, where, however, the doubling is probably due (cf. I, discussion of violet CN bands, pp. 485-6) to a double sign of ρ (F_1 and F_2 states). In the case of σ-type doubling, the two rotational states will now be designated F_A and F_B.

[3] The significance of these will be discussed in a subsequent paper.

As discussed in connection with CuH in I (pp. 498-9), ^1S states, where $\sigma=0$, show no rotational doubling. One might then expect ^1S rotational states to act, in their combinatory properties with ^1P states, like a coalescence of F_A and F_B states. Actually, however, they are *unsymmetrically* single in that they give Q combinations only with F_A states and P or R combinations only with F_B states, as expressed in Eqs. (1) and Fig. 1. These rules of combination are in fact here used as the basis for the *definition* of F_A and F_B states. This definition is intended to be so chosen that usually in practice $F_A(j) > F_B(j)$, to a certain extent paralleling the empirical relation $F_1(j+1) > F_2(j)$ which normally holds (cf. I,

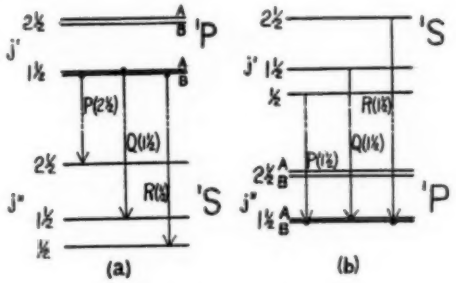

Fig. 1. Rotational energy levels and transitions for $^1S-{}^1P$ and $^1P-{}^1S$ electronic transitions. Only the lowest two or three levels are shown for each state. The only rotational transitions shown are those corresponding to the *first* possible line of each branch; additional band-lines are determined by analogous transitions between higher rotational levels.

p. 486) for ρ-type terms when $\epsilon=\frac{1}{2}$; the relation $F_A(j) > F_B(j)$ is illustrated by the He_2 bands (cf. Eqs. 1 and 2 and ρ and B values of Table I), but for the AlH bands (cf. Eq. 4) $F_B(j) > F_A(j)$. In view of their combinatory properties, ^1S states are classified as F_B states.[4] $^1S-{}^1S$ transitions, which might legitimately be included as special cases under the present discussion, have already been sufficiently treated in I (cf. pp. 498-500 and Eqs. 17).

$$^1S-{}^1P:\ R(j)=F_B'(j+1)-F_B''(j);\ Q(j)=F_A'(j)-F_B''(j);\qquad (1a)$$
$$P(j)=F_B'(j-1)-F_B''(j)$$

[4] In $^1S-{}^1S$ transitions it is practically certain that "crossing over" does not occur for the P and R branches, since the terms are single and presumably of the same rotational type for all ^1S states. But in other transitions there is no *direct* evidence at present against the possibility that it is really the P and R branches, instead of the Q branches for which crossing-over should be indicated in Eqs. (1) and (2); definite evidence could perhaps be obtained by a careful study of $He_2\lambda5733$. However, the analogy of the $^1S-{}^1S$ (and $^3S-{}^3S$, cf. I, p. 487) cases makes this very improbable, and it will therefore be assumed that crossing over occurs only in Q branches. A consequence of this assumption is the definite classification of ^1S states as F_B states.

$$^1P-{}^1S:\ R(j)=F_B'(j+1)-F_B''(j);\quad Q(j)=F_B'(j)-F_A''(j);\qquad (1b)$$
$$P(j)=F_B'(j-1)-F_B''(j)$$

For the general case of combinations between two σ-type terms, Eqs. (2) are applicable (these equations also serve to *define* Q_{AB} and Q_{BA} branches):[5]

$$\begin{aligned} R_A(j)&=F_A'(j+1)-F_A''(j) \quad ; \quad R_B(j)=F_B'(j+1)-F_B''(j)\\ Q_{BA}(j)&=F_B'(j)-F_A''(j) \quad ; \quad Q_{AB}(j)=F_A'(j)-F_B''(j)\\ P_A(j)&=F_A'(j-1)-F_A''(j) \quad ; \quad P_B(j)=F_B'(j-1)-F_B''(j) \end{aligned} \qquad (2)$$

Eqs. (1) and (2) illustrate a characteristic peculiarity of Q branches,—a "crossing over" (adopting an expression due to Prof. R. T. Birge) from an F_A to an F_B term or vice versa.[4] A result of this is the occurrence of apparent "combination defects" when one attempts to obtain Δ_1F values by making use of P, Q, R combinations (as in Eq. (20) of I); only Δ_2F combinations (cf. Eq. (18) of I) can be directly obtained.—Similar crossing over in Q branches also occurs in other than pure σ-type bands (e.g. in the HgH type and probably[21] in the CH type bands).

The most usual difference between F_A and F_B terms is the occurrence of an apparent small "secondary" ρ which differs in numerical value (sometimes also in sign) for F_A and F_B.[6] In such cases the rotational term is therefore, strictly speaking, apparently of the *general* form of Eq. (8) of I, but the $\rho\sigma^2$ term (cf. Eq. (8*A*) of I) would usually be so small that it can be neglected. In addition to the occurrence of a small ρ, there is often an apparent slight difference in the B values for F_A and F_B terms; and sometimes there is even a slight difference in the electronic term values ($F(e)$ of Eq. 3 of I), as is shown by the work of Curtis

[5] What is essentially the term-scheme of Eq. (2) was first suggested by Mecke (Phys. Zeits. **26**, 219 (1925)) for $He_2\lambda5733$, except that Mecke implicitly assumed the terms to be of the ρ type.

[6] The small secondary ρ's which occur in σ-type terms are paralleled in the case of doubling of the true ρ type by small *deviations* of ϵ from exact half-integers or integers as shown especially by Birge (cf. National Research Council Report on molecular spectra); without such small deviations there would be in fact no obvious doubling (cf. I, p. 486, violet CN bands). Also for ^1S states, where approximately $\rho=\sigma=0$, a small ρ can occur (cf. I, ref. 52, CuH bands). It also seems possible (although not obviously open to experimental verification) that small secondary σ's sometimes exist in the case of ρ-type states, and that there may be small deviations of σ from exact integers or half-integers in σ-type states; these questions have been discussed to some extent previously in connection with the HgH type bands.[2]

It may be, however, that the use of a linear term in j, as introduced by Kratzer (cf. I, pp. 485–6), will prove to be more correct physically than the use of a "secondary ρ"; formally, the two are practically equivalent.

and Long on the He_2 bands (see below). $F(j)$ can then, formally at least, be represented by:

$$F_A(j) = B_A[(j-\rho_A)^2-\sigma^2]$$
$$F_B(j) = B_B[(j-\rho_B)^2-\sigma^2] \qquad (3)$$

CO *Bands*.[7] The Ångstrom CO bands have been discussed in I (pp. 501-2) and shown to fulfill all the requirements for a $^1P-{}^1S$ transition, except that Eqs. (1*b*) are replaced by simpler equations (Eqs. 19 of I) in which there is no separation of F'' into F_A'' and F_B''. We are free, however, to suppose that a very small separation is actually present, so that these bands need not be considered anomalous;[8] it is likely that the smallness of the separation is related to the high stability of the CO molecule; in the unstable He_2 molecule, especially for the more excited states (see below, Table I), the separations between F_A and F_B terms become very large.

The fourth positive bands of CO are without doubt due to a $^1S-{}^1P$ transition, as concluded by Birge (cf. I, Fig. 1); the structure of these bands has not been investigated in detail, but so far as it is known, seems to be in agreement with expectation.

The infra-red CO absorption bands should involve ^1S states only, since the normal state of CO is ^1S (cf. I, Fig. 1 and p.), and should therefore have the same structure as the infra-red HCl absorption bands.

AlH *Bands*.[7] A system of bands due[9] to AlH has recently been investigated by Mörikofer[10] and by Eriksson and Hulthén.[11] As analyzed by the latter investigators, the bands all have exactly the same structure as the Ångstrom CO bands, except for the missing lines, which agree

[7] Since $j_0=1$ for $^3P_1$ atomic states, it is possible that $\sigma=1$, $\rho=0$ holds for $^3P_1$ as well as for ^1P molecular states, so that $^1S-{}^3P_1$ and $^3P_1-{}^1S$ transitions might give the same band-structure (including missing lines) as $^1S-{}^1P$ and $^1P-{}^1S$ transitions,—hence that the CO, AlH, and He_2 bands might correspond to transitions of the former rather than of the latter types. But the suggested identity of structure seems doubtful; or if it did exist, it is likely that $^1S-{}^3P_1$ combinations would be accompanied by $^1S-{}^3P_0$ (possibly also $^1S-{}^3P_2$) combinations which would betray them. In the cases of CO (cf. I, Fig. 1 discussion and ref. 38) and He_2 (cf. ref. 21 below), there is furthermore definite evidence against the presence of ^3P states for the bands here discussed.

[8] Dr. E. Hulthén has been so kind as to inform the writer that the Q branches finally begin to show slight combination defects for high values of j, thus showing that F_A'' and F_B'' are really distinct as expected.

[9] That the bands are due to AlH is sufficiently well shown by the experimental conditions (Al arc in H_2; also in absorption, in Al vapor plus H_2, according to Hulthén and Zumstein, Phys. Rev. **28**, 23 (1926)), and by the small moment of inertia disclosed by their analysis.

[10] W. Mörikofer, Dissertation Basel, 1925.

[11] G. Eriksson and E. Hulthén, Zeits. f. Physik **34**, 775 (1925).

perfectly[12] with Fig. 1*a* ($^1S-{}^1P$ transition), and except for the fact that the Q branches show apparent combination defects indicating that $F_A' \neq F_B'$.[13] The difference between F_A' and F_B' is apparently chiefly in the B values, since an approximate evaluation of the F's from Eriksson and Hulthén's data, assuming Eq. (1*a*), gives, for the band involving vibrational states having $n'=0$ and $n''=0$:

$$F_A' = 5.935(j^2-1) + \cdots ; \quad F_B' = 6.00(j^2-1) + \cdots ; \quad F'' = 6.29j^2 + \cdots \quad (4)$$

The He_2 *Bands.*[7] In all the He_2 bands,[14,15,16] the T values are apparently quarter-integral, while ΔT has the apparent values, $-\frac{1}{2}$, 0, and $+\frac{1}{2}$, for P, Q, and R branches. But on this basis, the branches which occur appear to be determined by arbitrary and mysterious selection principles. Besides this, there are missing in the λ5733 band two lines, $P'(2)$ and $Q_1(2)$ in Kratzer's numeration, whose absence is not accounted for.

An important clue to the understanding of these bands is the phenomenon of alternating intensities in band lines. This seems to be an exclusive characteristic of molecules composed of two like atoms.[17] Such alternating intensities occur in the second positive N_2, the N_2^+, in certain H_2, and doubtless in other bands.[18] In the Swan (probably C_2) bands, there are three R branches, in each of which, however, alternate lines are slightly displaced, so that each branch must be divided[19] into two series, of doubled spacing. Similar statements hold for the P branches (Q branches have not been observed). In explanation, Heurlinger suggested[19] that each individual series may be thought of as consisting of an alternation of strong and vanishingly weak lines, so placed with respect

[12] According to Mörikofer, a number of additional lines are present in some of the bands, corresponding to smaller values of j (in some cases negative!) than those noted by Eriksson and Hulthén; but for the most part these are discontinuously weaker than preceding members of the series. Eriksson and Hulthén state that each branch always begins with a strong line, and on the whole it seems legitimate to leave out of account the additional lines noted by Mörikofer.

[13] Except for the missing lines, which indicate a ^1P *initial* state, it might be the final instead of the initial states which are double,—as indeed Eriksson and Hulthén supposed.

[14] W. E. Curtis, Proc. Roy. Soc. **101**, 38 (1922): λ5733, 6400 and 4546 bands.

[15] "Series Bands," W. E. Curtis, Proc. Roy. Soc. **103**, 315 (1923); W. E. Curtis and R. G. Long, Proc. Roy. Soc. **108**, 513 (1925). In these bands, combination relations do not exist between the Q branches and the P and R branches (the usual relations exist between the P and R branches). Curtis and Long, however, assume that all three branches are associated with a *common set* of *final* rotational states; this assumption has been adopted here.

[16] A. Kratzer, Zeits. f. Physik **16**, 353 (1923).

[17] Cf. R. Mecke, Zeits. f. Physik **31**, 709 (1925).

[18] Cf. R. Mecke, Phys. Zeits. **25**, 1 (1924); Zeits. f. Physik **28**, 269 (1924).

[19] T. Heurlinger, Dissertation Lund, pp. 46–47 and 52–53 (1918).

to those of the companion series that the strong lines of the one series alternate with those of the other to make the almost-continuous composite series which corresponds to an observed branch (this will be made clearer by an examination of one of the series (of doublets) for the case

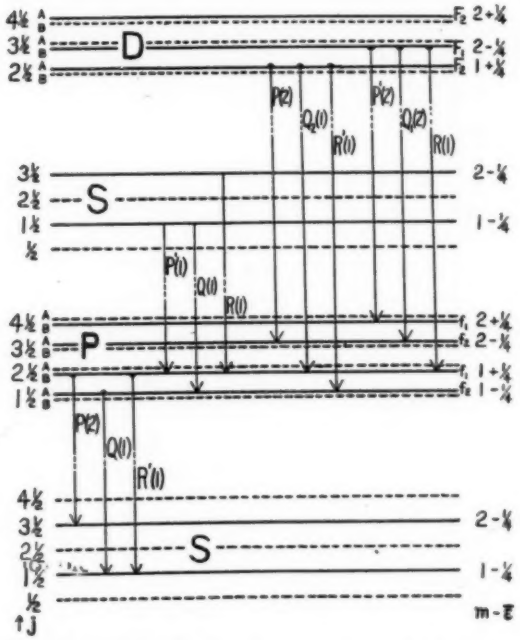

Fig. 2. Rotational energy level schemes for ^1S, ^1P and ^1D electronic states in He_2, and rotational transitions corresponding to first observed line of each branch (cf. description of Fig. 1) for $^1S-{}^1P$, $^1P-{}^1S$ and $^1P-{}^1D$ combinations. The spacing of the rotational levels is *not to scale*.

The full lines represent levels between which combinations have actually been observed, while the dashed lines correspond to hypothetical intermediate levels whose suppression is probably somehow related to the symmetry of the molecule (cf. refs. 17, 19 and 20). The complete absence of levels having $j=\frac{1}{2}$ in the case of P states, and of levels having $j=\frac{1}{2}$ or $1\frac{1}{2}$ in D states, is ascribed to the presence of a σ ($\sigma=1$ for P states, and $\sigma=2$ for D states), and is perhaps the strongest argument from the band structure for the designations P and D. The missing lines, and the first lines which are present in each branch, are determined by both these types of missing levels jointly.

At the left of the figure are the j values as here assigned, and the classification of the rotational levels as A or B (for ^1S states all the levels are classed as B levels). At the right, for convenience of comparison, are Kratzer's designations for the two observed classes of rotational levels in P and D states, together with his assignment of m and $\bar{\rho}$ values. (In the figure, was $\bar{\epsilon}$ inadvertently used instead of $\bar{\rho}$). The designations given for the first observed lines of each branch are in the notation and numbering of Kratzer and Curtis (the *number* in each case is merely the value of Kratzer's m'').

The suppressed levels can be summarized as follows: B levels, $\frac{1}{2}$, $2\frac{1}{2}$, $4\frac{1}{2}$, $\cdots$ for S states, $1\frac{1}{2}$, $3\frac{1}{2}$, $5\frac{1}{2}$, $\cdots$ for P states, and $2\frac{1}{2}$, $4\frac{1}{2}$, $6\frac{1}{2}$, $\cdots$ for D states; A levels, $2\frac{1}{2}$, $4\frac{1}{2}$, $6\frac{1}{2}$, $\cdots$ for P states, $3\frac{1}{2}$, $5\frac{1}{2}$, $\cdots$ for D states.

marked $^1P-{}^1D$ in Fig. 3 below). If the alternate weak members in each individual series were *not vanishingly* weak, each branch would consist of narrow doublets, of which alternately the high- and the low-frequency component would be the more intense. Exactly this condition is observed in the second positive nitrogen bands, whose structure is identical[19] with that of the Swan bands if Heurlinger's suggestion of alternate missing lines is adopted for the latter.—A suggestion in regard to the cause of such alternating intensities has been made by Slater.[20] The problem has been considered recently by Van Vleck (Phys. Rev., Nov., 1926).

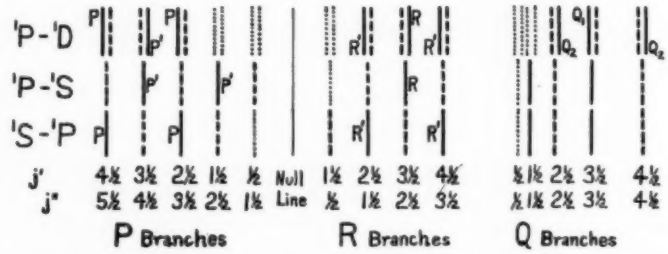

Fig. 3. Diagrammatic representation of arrangement of band lines for the three known types of He_2 bands. To avoid confusion the Q branches are drawn separately from the P and R branches. For simplicity the latter are drawn as if given by equations of the form $\nu = A \pm Bj''$; actually there should in general be a slight discontinuity at the null line, corresponding to a small difference in the A values for the P and R branches (cf. Eq. (5) of *I*); and of course there should be terms in j''^2, j''^3, etc., in the ν expression.

In the diagram the full lines represent observed band lines, the dashed lines correspond to "alternate missing lines," while the dotted lines indicate "central missing lines," i.e., band lines which are missing due to the condition that j cannot be less than σ. The occurrence of only three branches for $^1S-{}^1P$ and $^1P-{}^1S$ transitions, but six for $^1P-{}^1D$ transitions, is due to the singleness of the ^1S rotational states, as explained in the text.

If the dashed lines in Fig. 3 be converted into full lines, the diagram becomes identical with that for *ordinary* $^1S-{}^1P$, $^1P-{}^1S$, and $^1P-{}^1D$ transitions, as in AlH, CO, etc.

Mecke has pointed out[21] that the peculiarities of the He_2 bands largely disappear if one assumes alternate lines to be missing in each branch (as in Heurlinger's interpretation of the Swan bands). Applying this suggestion,[22] by assuming suitable sets of *alternate suppressed rotational*

[20] J. C. Slater, Nature **117**, 555, April 17 (1926).

[21] R. Mecke, Phys. Zeit. **26**, 227 (1925).

[22] Adopting a suggestion rejected by Mecke,[17,18] Dieke has proposed the subdivision of each alternating series in N_2^+ into two series composed respectively of the strong and of the weak lines (G.H. Dieke, Zeits. f. Physik **31**, 326 (1925)). This, however, gratuitously introduces[17] into the interpretation of the N_2^+ bands the peculiarities of the He_2 bands, and is open to other objections, e.g., the B values are four times as large as according to the other interpretation, and much larger than for related molecules such as CN and CO. This change in the values of B and other coefficients in the expression for $F(j)$ permit a critical test, however: as Birge has shown (R. T. Birge, Nature **116**, 783 (1925)), the experimental ω_0 values agree with the theoretical relation (cf. below,

energy levels, it becomes evident that the "series bands"[15] are of exactly the same type (three branches, combination defects in P–Q–R combinations,[15] etc.) as the $^1S-{}^1P$ AlH bands, while the bands λ4546 and λ6400 fall at once under the $^1P-{}^1S$ type. The band λ5733, which has the same final state as λ4546 and λ6400,[16] differs from all the other known He_2 bands in having six branches (and in being shaded toward the violet), and also has more missing lines per branch than any of the other He_2 bands. The missing lines, hitherto not explained, are on the new basis exactly those to be expected for a $^1P-{}^1D$ transition ($\sigma'=2$, $\sigma''=1$). This band now constitutes the typical example of the general case of a combination of two σ-type terms in agreement with Eq. (2), and furnishes in fact the experimental basis for Eq. (2).[5] It also shows definitely, by elimination, that it is the ^1S state which is responsible for the fewness of branches and other peculiarities of $^1S-{}^1P$ and $^1P-{}^1S$ combinations.

The relations stated in the preceding paragraph will become clear by a study of Figs. 2 and 3.

Starting with the assignment of electronic term designations just arrived at, strong evidence for their correctness was given in a previous paper,[23] to which reference should be made, on the ground of series relations of the electronic terms (supplementing the work of Fowler and of Curtis and Long); this evidence may now fairly be cited on its own merits as giving support to the interpretations here given of the *structure* of the He_2 bands. There is, furthermore, direct evidence (see below) in favor of the scheme of rotational levels given in Fig. 2, and in addition, the new interpretation leads to more reasonable B and ω_0 values than the old (cf. refs. 23 and 23a, also Table I, p. 1215); all this is in addition to the satisfactory explanation of the band structure.

In the above-mentioned paper,[23] it was shown that the electronic terms in the "main series"[15] and related bands (λλ6400, 4546, 5733) parallel the "doublet" (presumably triplet) terms of the He atom, while the electronic terms of the "second series"[15] bands parallel the singlet terms

p. 1214) $\omega_0=\sqrt{4B^3/\beta}$ only if the alternate strong and weak members of each otherwise continuous series are assumed, contrary to Dieke's interpretation, to belong physically to a single series. Hence the assumption of the extreme case of alternating intensity, i.e., alternate missing lines, in the Swan bands and in the He_2 bands, cannot be considered a radical one.

[23] R. S. Mulliken, Proc. Nat. Acad. Sci. **12**, 158 (1926). The writer wishes to express here his regret at having failed to notice until recently a paper by Y. Takahashi (Jap. J. of Physics **2**, 103 (1923)) in which electronic term designations for the He_2 bands were proposed, in part similar to those arrived at later by the writer. Attention may also be called to Curtis and Long's discussion of the nature of the terms and of the emitting molecule (l.c., ref. 15, pp. 533–38).

[23a] R. Mecke, Zeits. f. Physik **32**, 823 (1925).

of the atom. In explanation it was suggested that the "main series" is emitted by molecules composed in their least excited state of two He atoms each in the metastable $2\,^3S$ state, and the less prominent "second series" by more loosely bound molecules composed of two atoms each in the metastable $2\,^1S$ state. In the former case ($2\,^3S$, $2\,^3S$), the resultant molecular ^1S state ($j_e=0$) must evidently arise from an interaction and mutual neutralization of the j_e's of the two atoms ($j_e=1$ for each), while in the latter case ($2\,^1S$, $2\,^1S$), with $j_e=0$ for each atom, no interaction is needed to give the ^1S molecular state.[24] The conceivable case ($2\,^1S$, $2\,^3S$) seems not to be present in bands now known, while the cases ($1\,^1S$, $2\,^3S$) and ($1\,^1S$, $2\,^1S$) may fairly safely be left out of consideration in view of the inertness of the normal ($1\,^1S$) state of the He atom. The known *excited* electronic states of the He_2 molecule presumably correspond to the excitation of an electron (above the $2\,S$ state) in one atom only, to electronic states belonging to the same system (triplet for the main series, singlet for the second series) as for the corresponding least excited state of the molecule. This accounts for the marked resemblance of the molecular *term values* to those of corresponding atomic terms. But in spite of this resemblance the *multiplicity* is completely changed, in the case of the molecular forms composed of two triplet atoms, by the interaction of the two atoms.

The direct evidence for the alternate missing level scheme of Fig. 2 is as follows. In Fig. 2 the arrangement of the missing levels differs for ^1S, ^1P, and ^1D states; but for *all the states of each type* the same characteristic arrangement must exist. This is shown for ^1S states by the identical structure of the two bands λ6400 and λ4546 ($2P-3S$ and $2P-4S$),[23] and for ^1P states by the identical structure of all members of the series $2S-mP$,—for both "main" and "second" series. From the scheme of levels in Fig. 2, it can then readily be seen that P and R branches should be impossible in $^1S-{}^1S$ transitions, while Q branches are not to be expected, since they are absent in known $^1S-{}^1S$ transitions (CuH, etc.). Similarly, P, Q, and R branches should all be impossible (assuming Eq. 2) in $^1P-{}^1P$ (and $^1D-{}^1D$) transitions, as can be seen from the figure.

[24] That the known molecular electronic states are all of a singlet type is fairly satisfactorily shown by the comparative simplicity of the band structures; if any of the bands involved triplet terms, a corresponding multiple ν^σ would be expected, at least in the case of λ6400, 4546 and 5733, whose common final $2P$ state, if it were ^3P rather than ^1P, should probably be resolved, since in the atom the $2\,^3P$ ($2P$ "doublet") state shows an appreciable separation into (apparently two) components; or if an electronic fine structure were present but unresolved, it should still make itself felt by the occurrence of more than one value of σ, with a corresponding change (reduction) in the number of missing lines,—and also perhaps in other ways.

There is no reason to expect these transitions to be barred as in line spectra by a selection principle, since intense $S-S$ and $P-P$ combinations are known for other molecules. It then seems very significant that no He_2 bands corresponding to either $^1S-{}^1S$ or $^1P-{}^1P$ transitions are known. Dr. Curtis has recently re-examined his plates and has been so kind as to inform the writer that he finds no evidence of any of the combinations $2S-3S$, $2S-4S$, $2P-3P$, $2P-4P$, although if present, their location is such that they should all have been rather easily detected. This result gives strong support to the missing level scheme of Fig. 2.[25]

The new interpretation of the He_2 bands here proposed requires a re-interpretation of ΔF values and a corresponding re-evaluation of coefficients. In general for any band spectrum, the ΔF's, when correctly evaluated by means of combination relations (cf. I, p. 490), are empirical quantities which are unalterable by any change of theory (other than a loss of faith in the combination principle). The determination of F's from ΔF's depends, however, on additional theoretical considerations. In the present case, the change in the theory introduced is fortunately of such a character that the new F's can be obtained from the old F's of Kratzer and Curtis and Long by a simple transformation, without the necessity of going back to the original ΔF values. (This can be seen by an examination of the definition of ΔF in relation to the following equations.)

For the F values, Kratzer[16] assumed in effect the following form; in this equation $M=m-\bar{\rho}$, and $M^*=m-\bar{\theta}$ (the notation here used differs from Kratzer's):

$$\bar{F}(M)=\bar{B}M^2-\bar{\beta}M^{*4}+\cdots \tag{5}$$

In Eq. (5) Kratzer *assumed* m (not M) to be integral, and then found $\bar{\rho}$ to have approximately the values $+\frac{1}{4}$ and $-\frac{1}{4}$; $\bar{\theta}$ is a quantity of the same sign as $\bar{\rho}$ but differing considerably from $\bar{\rho}$, according to Kratzer's analysis, in numerical value.[26]

[25] Except for this evidence, the observed facts could be accounted for in either of two other ways which represent modifications of the scheme of alternate missing levels given in Fig. 2: it can be assumed (1) that *all* the rotational levels are present for the D states, but that alternate levels are missing as in Fig. 2 for the S and P states (an additional possibility scarcely worth mentioning is that the S levels, *except* $j=\frac{1}{2}$, are all present, either instead of, or in addition to, the full set of D levels); or (2) that all the rotational levels are present for P states, but that alternate levels are missing as in Fig. 2 for S and D states. Neither of these is very plausible, and at least the second of the two possibilities (as also the possibility that all or all but one of the rotational levels are present for S states) seems to be definitely negatived by the evidence given in the text.

[26] It should be remarked that m as used by Kratzer was *intended* by him to be identical in significance with j as here used, although in the revised interpretation of the He_2 bands here proposed this is not the case.

The assumption of alternate missing lines and rotational levels means that the succession of observed M values, M_0, M_0+1, M_0+2, $\cdots$, is to be interpreted as corresponding to alternate members $2M_0$, $2M_0+2$, $2M_0+4$, $\cdots$, of a succession of values $(2M_0-1)$, $2M_0$, $2M_0+1$, $\cdots$, the levels corresponding to $(2M_0-1)$, $2M_0+1$, $2M_0+3$, $\cdots$, being assumed to be suppressed (at least in respect to the emission of radiation). Since the M's always have approximately quarter-integral values, the $(2M$'s) all have approximately half-integral values; according to the present interpretation, $2M$ is to be identified with T. But the f *values* should be half-integral for He_2, since it is an even molecule (cf. I, postulate *III*). Since T, which is necessarily equal to $j-\rho$ if the rotational terms are essentially, as we assume, of the Kramers and Pauli form, is approximately half-integral, we conclude that $T\sim j$, and $\rho\sim 0$, the usual small deviations of T from exact half-integral values being ascribed to small "secondary" ρ's. The resulting interpretations are then in harmony with those already adopted for the CO and AlH bands.

In terms of T, Eq. (5) can now be rewritten

$$\bar{F}(T)=(\bar{B}/4)T^2-(\bar{\beta}/16)T^{*4}+\cdots \tag{6}$$

Then, putting $\bar{\beta}/16=\beta$ and $(\bar{B}/4)-2\beta\sigma^2=B$, and neglecting the difference between T and T^*[27], and adding the experimentally not directly detectable small terms $-B\sigma^2$ and $-\beta\sigma^4$, Eq. (6) can be reduced to the following form, which is merely Eq. (3) with the addition of the next higher power term as obtained by Kemble:[28]

$$F(j)=B[(j-\rho)^2-\sigma^2]-\beta[(j-\rho)^2-\sigma^2]^2+\cdots \tag{7}$$

Here ρ is related to $\bar{\rho}$ by the equation $\rho=2\bar{\rho}\pm\frac{1}{2}$, the upper sign for $\bar{\rho}$ negative, the lower for $\bar{\rho}$ positive. The values of B, β, and ρ for each electronic state can now be obtained by simple calculation from the values given by Kratzer and Curtis and Long.[27] The vibration frequencies also, although not directly observed, can probably be approximately calculated by means of the theoretical relation[29] $\omega_0=\sqrt{4B^3/\beta}$. The values of ω_0

[27] Strictly, of course, the constants (especially β) should be re-evaluated from the original data, but this will not be attempted here.

[28] In the forthcoming National Research Council Report on Molecular Spectra, Kemble shows that the complete Kramers and Pauli term (Eq. (8) of *I*) has the form $F(j)=Bm^2-\beta m^4+\cdots$, with $m=\sqrt{j^2-\sigma^2}-\rho$ as in Eq. (8) of *I*. The corresponding completed form of Eq. (3) is Eq. (7).

[29] Cf. A. Kratzer, Ann. der Physik **71**, 80 (1923). The relation is strictly applicable only when $n=0$ (E. C. Kemble, J.O.S.A. **12**, 1 (1926); β as used here is Kemble's D); fortunately the known He_2 bands probably all have n' and n'' equal to zero.

previously calculated by Kratzer and Curtis and Long must be approximately halved, since $\sqrt{4B^3/\beta} \sim \frac{1}{2}(\sqrt{4\overline{B}^3/\overline{\beta}})$.

The He_2 bands now illustrate well the phenomenon of rotational doubling for σ-type terms. Accordnig to Curtis and Long's analysis of the bands of the "main series," the ρ values for the $3P$ electronic state are small or negligible, and the ν^e and B values are practically the same for F_A and F_B states; but for more and more excited P states, a progres-

TABLE I

Constants of molecular helium in various electronic states

El. State[22]	B_A	B_B	ρ_A	ρ_B	$\beta_A \times 10^4$	$\beta_B \times 10^4$	ω_0	r_0(A.U.) A	B
				A. Main series and related bands					
$2S$	7.589		.001		5.51		1780	1.050	
†$3S$	7.21		0		....		....	1.079	
†$4S$	7.13		0		....		....	1.084	
†$2P$	7.320	7.320	−.004	.004	5.08	5.08	1760	1.070	
$3P$	7.175	7.102	.003	0	5.17	5.01	1690	1.081	1.086
$4P$	7.140	6.966	.005	0	5.32	4.48	1700	1.084	1.098
$5P$	7.130	6.944	.013?	.066?	5.33	4.65	1680	1.084	1.100
$6P$	7.116	6.722	.004	.042	5.32	4.31	1670	1.085	1.117
$7P$	7.117	6.637	.006	.092	5.45	....		1.085	1.124
$8P$	7.111	6.646	.005	.222	5.37	....		1.086	1.122
$9P$	7.14	.....	.01	....	8.5			1.084	
$10P$	7.18	.....	.02	....	11.3			1.081	
†$3D$	7.555	7.555	−.003	.003	7.37	7.37	1530	1.052	
				B. Second series.					
$2S$	7.65		.00					1.047	
$3P$	7.17	7.12	.02	.02				1.08	1.08
$4P$	7.11	6.97	.00	−.02				1.09	1.10
$5P$	7.17	6.74*	.06*	−.14*				1.08	1.12
$6P$	7.18	6.60*	.05*	−.19*				1.08	1.13

Notes: (1) the values of ω_0 (the vibration frequency) are average values calculated from both F_A and F_B terms. (2) r_0 is the internuclear distance, calculated from B. (3) The data for the states marked † are from Kratzer's analysis, the remaining data from Curtis and Long's work. On account of certain differences in the method of analysis, the two sets of data are not strictly comparable. In particular, the opposite signs and equal magnitudes of ρ_A and ρ_B, and the exact equalities of B_A and B_B, and of β_A and β_B, for the $2S$ and $3D$ terms, are not significant, since they were in effect *assumed* by Kratzer as a part of the theoretical preliminaries to the determination of constants to fit the observed data. Also, (even the mean) β and ω_0 values of Kratzer and of Curtis and Long are not exactly comparable, since Kratzer assumed M and M^* of Eq. (5) to be distinct, while Curtis and Long assumed them identical. (4) It is not certain that the negative ρ_B values for the P terms of the second series are significant, since no great accuracy is claimed for the analysis (this is especially so in the cases marked*)

sively increasing separation between the F_A and F_B states develops, so that for the most excited P states the ρ_B values are large, and the B_B values are much less than for the $3P$ state, while the ρ_A values remain small, and B_A falls only slightly with increasing electronic excitation. This striking difference in behavior of F_A and F_B terms should be of assistance in determining the nature of the σ type of rotational doubling.

The ρ, B, and ω_0 values for all known electronic states of He_2 are given in Table I; these values are essentially results of the work of Curtis and Long and of Kratzer, having been subjected here, without re-examination of the original data, only to the simple transformations indicated in connection with Eqs. (6) and (7). For the ν^e values, reference should be made to Curtis and Long's and Kratzer's papers (the values given by these authors should of course be slightly altered, essentially by the amount of the appropriate $B\sigma^2$ terms).

Alkali metal bands. All the alkali metals show band absorption spectra which are commonly attributed to diatomic molecules Na_2, K_2, etc. This is justified by the close spacing of the band lines,[30,31] the very low vibration frequencies,[32] and especially by the fact that similar but new and characteristic spectra (e.g. the NaK bands) appear in mixed alkali metal vapors.[31,33]

No satisfactory analysis of any of these bands, making use of combination relations, has been carried through, although Smith[31] has arranged a number of the Na_2, NaK, and K_2 bands, mostly in three branches (P, Q, and R). But from R. W. Wood's work on the "resonance spectra" excited in sodium vapor by monochromatic light, it seems fairly clear, as will be shown, that the yellow and green Na_2 bands[32] are due to a transition $^1S-{}^1P$ like the AlH bands.

Let us assume for the time being the correctness of this characterization. Sodium molecules in a variety of vibrational and rotational states of the ^1S electronic state should then be present in the heated absorption tube (temperature about 400°C in Wood's experiments). If the vapor is illuminated with monochromatic light of suitable wave-length, molecules in one of these states will be enabled to go to a particular vibrational and rotational state belonging to the ^1P excited electronic state. If the

[30] R. W. Wood, Physical Optics, pp. 571-79, 1919 ed.

[31] H. G. Smith, Proc. Roy. Soc. **106,** 400 (1924).

[32] An inspection of Wood's Fig. 350 (ref. 30, p. 574) shows that the green and yellow Na_2 absorption bands together form a typical band-system. This can easily be seen by comparison with e.g., the writer's photograph (Phys. Rev. **26,** 1, (1925)) of the green CuI bands (A bands). The arrangement and vibrational intensity distribution in the Na_2 bands are closely similar to those in the A bands of CuI. From Wood's figure it can also be seen that n'' reaches values as high as 15, while n' also reaches fairly high values.—The vibration frequency ω_0'' for the final state can be obtained approximately from Wood's Na_2 resonance series, being roughly equal (in wave-number units) to the spacing of the two highest-frequency members of any such series. This procedure yields $\omega_0'' \sim 150$. From the structure of the absorption spectrum (cf. Wood's Fig. 350), it is then possible to deduce $\omega_0' \sim 127$.

[33] S. Barratt, Proc. Roy. Soc. **105A,** 221 (1924); F. H. Newman, Phil. Mag. **48,** 159 (1924); P. Pringsheim, Zeits. f. Physik **38,** 161 (1926), and refs. there cited.

absorbed light should correspond to a Q branch line, the molecule goes to an F_A rotational state, if to either a P or an R line, it goes to an F_B rotational state (cf. Fig. 1*a*). From an F_B excited state the molecule can return by either a P or an R transition ($\Delta j = -1$ or $+1$) to any vibrational level of the normal electronic state of the molecule; this process should give rise to a typical series of "resonance doublets" (as in the I_2 bands[34]), the different doublets in the series corresponding to different final vibrational states of the molecule. But from an F_A rotational state the molecule can return only by a Q transition ($\Delta j = 0$), so that here the resonance series should consist of a set of single lines.

For a $^1P - {}^1S$ transition, on the other hand, the resonance series should all consist of *triplets* (P, Q, R), as can be seen by a study of Fig. 1*b*; the same is true of a $^1P - {}^1D$ or $^1D - {}^1P$ transition, as can be seen by consideration of Eq. (2). For a $^1S - {}^1S$ transition, *doublet* series *alone* are to be expected, since only P and R transitions occur in such bands; the resonance spectrum of I_2, as investigated by Wood and interpreted by Lenz,[34] appears to be of this type.[35] In the case of a $^1P - {}^1P$ (or $^1D - {}^1D$) transition, resonance triplets are to be expected (cf. Eq. 2), but should appear in practice as doublets, since for such transitions the Q branch should be much weaker and shorter than the P and R branches (as is shown by an application of the correspondence principle, discussed in III of this series). The I_2 bands might be of such a type,[35] if it were not that I_2 vapor is probably (by analogy with Cl_2 gas) diamagnetic; this indicates a ^1S normal state (cf. I, p. 504), and so seems to rule out $^1P - {}^1P$ here in favor of $^1S - {}^1S$.

The work of Wood and Hackett on the green Na_2 absorption bands shows[30] that some absorbed wave-lengths (e.g. Cd λ4800) give rise to resonance series composed of single lines, others (e.g. Cd λ5086) to series composed of doublets. Since this behavior agrees with that predicted

[34] W. Lenz, Phys. Zeits. **21**, 691 (1920). Cf. A. Sommerfeld, Atombau und Spektrallinien, 4th Ed., pp. 725–26, for brief discussion. Cf. also E. C. Kemble and E. E. Witmer, Phys. Rev. **28**, 633 (1926).

[35] Since I_2 and Na_2 are each composed of two like atoms, the suppression of alternate rotational levels (partial as in N_2 and N_2^+, or complete as in He_2) is likely, for some at least of the electronic states of these molecules. A study of Fig. 2 will show, however, that the nature (doublets, triplets, or singlets and doublets) of the resonance series to be expected, for any type of electronic transition, would be unaffected by this circumstance (except for the one special case of $j' = 1\frac{1}{2}$, for a $^1P - {}^1S$ transition). Absorption and resonance would, however, be completely suppressed for $^1S - {}^1S$, $^1P - {}^1P$, or $^1D - {}^1D$ combinations (cf. above, p. 1213) in case the suppression of alternate rotational levels is complete in *both* upper and lower electronic states; the latter condition therefore probably does not exist in the case of I_2.

for a $^1S-{}^1P$ transition and for no other,[35,36] it is probable that the Na_2 band-system[32] in this region is of this type. It is likely that the red Na_2 system, as well as other systems further in the ultra-violet, are of the same type. If so, the various excited ^1P states are probably due to a rather loose union of a normal ($3\,{}^2S$) and an excited ($m\,{}^2P$) Na atom, and the normal ^1S molecular state to a similar union of two normal atoms.[37] The red bands may be $3\,{}^1S-3\,{}^1P$ (corresponding to the D lines of the Na atom, but, as expected, lacking the doublet character of the latter, of which there seems to be no evidence in any of the Na_2 bands), and the yellow and green bands $3\,{}^1S-4\,{}^1P$. So far as they are known, the NaK, K_2, and other alkali metal absorption bands are all closely analogous to the Na_2 bands, and so presumably correspond to the same type of electronic transition.[36]

B. Spectra of Molecules with an Odd Number of Electrons

$^2S-{}^2P$ and $^2P-{}^2S$ combinations. In even molecules, as we have seen, $j_e=\sigma=1$ for ^1P states, while $j_e=0$ for ^1S states, and for both states $T=j=$half-integral. As a result, the band structure is comparatively simple in $^1P-{}^1S$ and $^1S-{}^1P$ transitions. For odd molecules, however, the band structure is necessarily more complicated in P–S transitions, according to the conclusions and postulates of I: in ^2S states, $j_e=\rho=\pm\frac{1}{2}$, while for ^2P states $j_e=\sigma$ ($\sigma=\frac{1}{2}$ for $^2P_1$ and $1\frac{1}{2}$ for $^2P_2$ states), so that $T=j\mp\frac{1}{2}=$half-integral for ^2S states but $T=j=$integral for ^2P states.

The only examples of $^2S-{}^2P$ transitions whose structure is known in detail are the ZnH, CdH, and HgH bands. The interpretation of these bands in agreement with the postulates of I (modifying Kratzer's previous interpretation) has been discussed in an earlier paper,[2] to which reference should be made. Due presumably to the fact that they involve both ρ-type and σ-type terms, the observed branches appear to be determined in a different way than for cases involving only σ-type terms as in Eqs. (1) above. Briefly, the behavior of the initial σ-type states here is such that the observed rotational doubling is more appropriately classified, like that of the final ρ-type states, in accordance with the ρ-type notation (F_1, F_2) than with the F_A, F_B notation of Eqs. (1) and (2). The Q branches, however, show crossing over as in Eqs. (1) and (2). Further details are given in ref. 2.

[36] It is, however, not out of the question that some other transition involving electronic terms of triplet or higher multiplicity might show the same behavior as $^1S-{}^1P$ (cf. ref. 7).—The occurrence of triplet states for alkali metal molecules is indeed likely, but there is no obvious evidence of it as yet.

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For $^2S-{}^2P_1$ and for $^2S-{}^2P_2$ transitions, the following equations hold (neglecting higher power terms), as is shown by the ZnH, CdH, and HgH bands:

$$\begin{aligned} &R_1(j-1), R_2(j-1) = \nu^0 + F_1'(j), F_2'(j) - B''(j-1\mp\epsilon)^2 \\ &Q_1(j), Q_2(j) \qquad\quad = \nu^0 + F_2'(j), F_1'(j) - B''(j\mp\epsilon)^2 \\ &P_1(j+1), P_2(j+1) = \nu^0 + F_1'(j), F_2'(j) - B''(j+1\mp\epsilon)^2 \end{aligned} \tag{8A}$$

Letting $\nu' = \nu^0 - B''\epsilon^2$, these give on expansion:

$$\begin{aligned} R_1(j-1) &= \nu' + F_1'(j) - B''(1+2\epsilon) + 2B''(1+\epsilon)j - B''j^2 \\ R_2(j-1) &= \nu' + F_2'(j) - B''(1-2\epsilon) + 2B''(1-\epsilon)j - B''j^2 \\ Q_1(j) \quad &= \nu' + F_2'(j) \qquad\quad + 2B''\epsilon j \quad - B''j^2 \\ Q_2(j) \quad &= \nu' + F_1'(j) \qquad\quad - 2B''\epsilon j \quad - B''j^2 \\ P_1(j+1) &= \nu' + F_1'(j) - B''(1-2\epsilon) - 2B''(1-\epsilon)j - B''j^2 \\ P_2(j+1) &= \nu' + F_2'(j) - B''(1+2\epsilon) - 2B''(1+\epsilon)j - B''j^2 \end{aligned} \tag{8}$$

Approximately, $F_1'(j) = F_2'(j) = B'(j^2-\sigma^2)$, and approximately, $\epsilon = \frac{1}{2}$. In general, these equalities are not exact, and there are six distinct branches, as in ZnH, CdH, and HgH. But in the special case that they *are* exact,[38] a complete coalescence of certain branches should occur. For this case, if $\bar{\nu}^0 = \nu^0 - B'\sigma^2 - B''\epsilon^2$ ($\sigma = \frac{1}{2}$ for a $^2P_1$, or $1\frac{1}{2}$ for a $^2P_2$, electronic state), and $C = B' - B''$, Eqs. (8) reduce to the form:

$$\begin{aligned} R_1(j-1) &= \bar{\nu}^0 - 2B'' + 3B''j + Cj^2 \\ R_2(j-1) = Q_1(j) &= \bar{\nu}^0 + B''j + Cj^2 \\ Q_2(j) \quad = P_1(j+1) &= \bar{\nu}^0 - B''j + Cj^2 \\ P_2(j+1) &= \bar{\nu}^0 - 2B'' - 3B''j + Cj^2 \end{aligned} \tag{8B}$$

Thus (cf. I, Eq. 5 and p. 492) the R_1 branch is 3/2-*R*-form, the R_2 and Q_1 branches are semi-*R*-form, the Q_2 and P_1 branches semi-*P*-form, and the P_2 branch 3/2-*P*-form.

So far as can be seen from the obvious structure and the fragmentary detailed evidence now available, the precise state of affairs[38] expressed in Eqs. (8*B*) actually occurs in the red CN, BOα, and CO^+ comet tail bands (all of which are $^2S-{}^2P$ transitions like ZnH etc., cf. I, Fig. 1). The condition $\epsilon'' =$ exactly $\frac{1}{2}$ which is necessary for Eqs. (8*B*) is probably met[39]

[38] The equality $F'(j) = B'(j^2-\sigma^2)$ is of course not necessary, so long as $F_1' = F_2'$; e.g., the presence of a secondary ρ as in Eq. (3) is permissible, provided this ρ, and also B', have the same values for F_1 and F_2.

[39] The red CN bands have the same final state (cf. Fig. 1 of I, discussion) as the violet CN bands. In ref. 13 of I it was stated that Birge has shown that $\epsilon'' =$ exactly $\frac{1}{2}$ for the latter. This definite statement is unfortunately in error, but the relation in question is nevertheless probable.

for a $^1S-{}^1P$ transition and for no other,[35,36] it is probable that the Na_2 band-system[32] in this region is of this type. It is likely that the red Na_2 system, as well as other systems further in the ultra-violet, are of the same type. If so, the various excited ^1P states are probably due to a rather loose union of a normal ($3\,{}^2S$) and an excited ($m\,{}^2P$) Na atom, and the normal ^1S molecular state to a similar union of two normal atoms.[37] The red bands may be $3\,{}^1S-3\,{}^1P$ (corresponding to the D lines of the Na atom, but, as expected, lacking the doublet character of the latter, of which there seems to be no evidence in any of the Na_2 bands), and the yellow and green bands $3\,{}^1S-4\,{}^1P$. So far as they are known, the NaK, K_2, and other alkali metal absorption bands are all closely analogous to the Na_2 bands, and so presumably correspond to the same type of electronic transition.[36]

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Thus (cf. I, Eq. 5 and p. 492) the R_1 branch is 3/2-*R*-form, the R_2 and Q_1 branches are semi-*R*-form, the Q_2 and P_1 branches semi-*P*-form, and the P_2 branch 3/2-*P*-form.

So far as can be seen from the obvious structure and the fragmentary detailed evidence now available, the precise state of affairs[38] expressed in Eqs. (8*B*) actually occurs in the red CN, BOα, and CO^+ comet tail bands (all of which are $^2S-{}^2P$ transitions like ZnH etc., cf. I, Fig. 1). The condition $\epsilon'' =$ exactly $\frac{1}{2}$ which is necessary for Eqs. (8*B*) is probably met[39]

[38] The equality $F'(j) = B'(j^2-\sigma^2)$ is of course not necessary, so long as $F_1' = F_2'$; e.g., the presence of a secondary ρ as in Eq. (3) is permissible, provided this ρ, and also B', have the same values for F_1 and F_2.

[39] The red CN bands have the same final state (cf. Fig. 1 of I, discussion) as the violet CN bands. In ref. 13 of I it was stated that Birge has shown that $\epsilon'' =$ exactly $\frac{1}{2}$ for the latter. This definite statement is unfortunately in error, but the relation in question is nevertheless probable.

(assuming the essential correctness of Kratzer's interpretation of the violet CN bands as discussed in I) in the case of CN, and so by analogy may be expected for BO, CO^+, etc. The fulfillment both of this relation and of the necessary exact equality of F_1' and F_2' may be attributed to the relatively high stability of the molecules in question (cf. discussion above under CO), which is in contrast to that of the loosely bound molecules of the ZnH type.

Baldet has concluded[40] that the comet tail bands of CO^+ consist of a weak R branch, two strong Q branches, and a weak P branch. This otherwise puzzling result finds obvious explanation in Eqs.(8B). Furthermore, Blackburn's work on these bands shows[41] that the two strong branches are related as a P and an R branch, but with ΔT (previously implicitly assumed[41] to be Δm as in bands of the violet CN or CuH type) equal to $\pm\frac{1}{2}$. Also, the analysis shows combination relations between these two strong branches which yield $\Delta_1 F'$s[42] giving T' = integral, T'' = half-integral.[41] All this is exactly what would be expected according to the present interpretation in terms of Eqs. (8B).

It should be emphasized that the success of Eqs. (8) in interpreting the structure of the ZnH, CdH and HgH bands is strong direct evidence for the reality of the double sign of ρ (as introduced by Kratzer), with $\epsilon \sim \frac{1}{2}$. Furthermore, the applicability of Eqs. (8B) to the red CN bands (assuming that it will be confirmed by a detailed analysis)[42a] will give assurance of the reality of $\rho'' = \pm\frac{1}{2}$ for the violet as well as for the red CN bands, since these have a common final electronic state (cf. Fig. 1 of I, discussion). The essential features of Kratzer's interpretation of the violet CN bands should thereby receive a direct justification which is not possible (cf. I, ref. 14) by a consideration of these bands alone.—As already mentioned in I (pp. 500-1), the CH bands, essentially as interpreted by Kratzer, give additional direct evidence for a ρ having the values $\pm\frac{1}{2}$.

For transitions $^2P_{1,2} - {}^2S$, as in the combination bands of BO and CO^+ and the third positive NO bands (cf. I, Fig. 1), the predicted branches are easily shown to be of the same general forms as in Eqs. (8), and a similar coalescence, here of the R_1 and Q_2, and of the P_2 and Q_1 branches, should take place if ϵ' = exactly $\frac{1}{2}$ and $F_1'' = F_2''$. Complete coalescence

[40] F. Baldet, Compt. Rend. **180**, 820 (1925).

[41] Cf. R. S. Mulliken, Phys. Rev. **26**, 565 (1925).

[42] The combinations can equally well be regarded as between R_2 and Q_2, or as between P_1 and Q_1, and so in either case yield $\Delta_1 F'$s (cf. *I*, p. 491), provided of course the necessary conditions (in particular $F_1' = F_2'$) for Eq. (8B) are met.

[42a] High dispersion photographs of these bands have been obtained, and their measurement is in progress.

is probably not to be expected, in the examples mentioned; narrow doublets should probably be present. The obvious structure of the bands above mentioned is of the predicted type, but no detailed analysis of any of them has yet been made.

Other combinations. For transitions such as $^2P-^2D$, $^2D-^2P$, $^2P-^2P$, etc., Eqs. (2) and (3) may be expected to hold, and the band-structures, except for the missing lines and the occurrence of *integral* T values, should be essentially the same as for $^1P-^1D$, $^1D-^1P$, $^1P-^1P$, etc. Predictions for specific cases are readily made; an example will now be given.

In $^2P_2-^2D_3$ or $^2P_1-^2D_2$ transitions, intense P, Q, and R branches are to be expected, with each line a doublet. For $^2P_2-^2D_3(\sigma'=2\frac{1}{2}, \sigma''=1\frac{1}{2})$, the j values $(j'\rightarrow j'')$ for the first lines of the various branches should be $R(3\rightarrow 2)$; $Q(3\rightarrow 3)$; $P(3\rightarrow 4)$, there being five missing lines in the otherwise continuous series formed by the P and R branches. For $^2P_1-^2D_2$ $(\sigma'=1\frac{1}{2}, \sigma''=\frac{1}{2})$, the structure should of course be the same, but with only three missing lines in the P and R branches,—$R(2\rightarrow 1)$, $Q(2\rightarrow 2)$, and $P(2\rightarrow 3)$ being the expected first lines.

C. Summary of Spectrum Interpretations Previously Given

In the following table, the interpretations of individual spectra given in this and the preceding paper are summarized for convenience of reference. In the table, each emitter or spectrum named is typical; additional representatives of each type are given following the table.

Table II

Structure types and their interpretation

Type	Spectrum	Branches	T'_{min}	T''_{min}	Electr. qu. nos. ρ'	σ'	ρ''	σ''	Electr. transitions
I	CuH	P, R (2)	$\frac{1}{2}$	$\frac{1}{2}$	0	0	0	0	$^1S-^1S$
IIa	AlH	P, Q, R (3)	$1\frac{1}{2}$	$\frac{1}{2}$	0	1	0	0	$^1S-^1P$
IIb	Ångstrom CO	P, Q, R (3)	$\frac{1}{2}$	$1\frac{1}{2}$	0	0	0	1	$^1P-^1S$
III	$He_2\lambda 5733$	P, Q, R (6)	$2\frac{1}{2}$	$1\frac{1}{2}$	0	2	0	1	$^1P-^1D$
IV	Violet CN	P, R (4)	$\frac{1}{2}$	$\frac{1}{2}$	$\pm\frac{1}{2}$	0	$\pm\frac{1}{2}$	0	$^2S-^2S$
Va	ZnH	P, Q, R (6)	1	$(\frac{1}{2})$	0	$\frac{1}{2}$	$\pm\frac{1}{2}$	0	$^2S-^2P_1$
		P, Q, R (6)	2	$(\frac{1}{2})$	0	$1\frac{1}{2}$	$\pm\frac{1}{2}$	0	$^2S-^2P_2$
Vb	NO 3rd positive (prediction)	P, Q, R (6)	$(\frac{1}{2})$	1	$\pm\frac{1}{2}$	0	0	$\frac{1}{2}$	$^2P_1-^2S$
		P, Q, R (6)	$(\frac{1}{2})$	2	$\pm\frac{1}{2}$	0	0	$1\frac{1}{2}$	$^2P_2-^2S$
VIIa	CHλ3900	P, Q, R (6)	$\frac{1}{2}$		$\pm\frac{1}{2}$	0	$\pm\frac{1}{2}$(?)	1(?)	$^1P-^1S$ in C atom(?)

Notes for Table II. (*a*) The T values given are *observed* values (except for H_2 and NO 3rd positive bands) *smoothed* to exact integers or half-integers; for the He_2 bands, the values given are *twice* the *apparent* values (cf. above). In Type Va the value $\frac{1}{2}$ of $T''_{min.}$ applies to F_1 terms (and corresponds to $j''=1$); for F_2 terms the *observed* value of $T''_{min.}$ in the HgH bands is $1\frac{1}{2}$ (also corresponding to $j''=1$); the absence in these bands of $F_2(T=\frac{1}{2}, j=0)$, which should be present according to the considerations of I (p. 489), was attributed in ref. 2 to the presence of a small σ.

Additional representatives of types given in Table II (brackets denote that the classification given is in the nature of a prediction based on incomplete information): Type I, AgH, AuH, and the [visible absorption bands of Cl_2, Br_2, I_2]; infra-red oscillation-rotation bands of HF, HCl, HBr, [CO] (except of course that there is no electronic change); Type IIa, [alkali metal absorption bands], [CO 4th positive bands], He_2 "main" and "second" series bands; Type IIb, He_2 λ6400 and λ4546; Type IV, N_2^+, AlO, [CO^+ negative Deslandres], [BOβ], and [SiN] bands; Type Va, CdH, HgH, [BOα], [red CN], [CO^+ comet tail]; and probably the [doublet alkaline earth halide bands]; Type *Vb*, [BO and CO^+ combination bands], [SnCl bands]; Type VIIa, OH bands ($^1P-{}^1S$ transition in O atom?),—but ρ'' and σ'' must be supposed to vary with j''; also CH λ4300 (perhaps $^1P-{}^3S$ transition in C atom), except that this band has 12 branches; the green MgH bands (transition $3\,{}^1S-3\,{}^3P_1$ in Mg atom, probably) may be classified under Type VIIb, resembling the OH and CH λ3900 bands except for a reversal of the rôles of initial and final electronic states; in all bands of Type VII, $\epsilon'\sim\epsilon''$ is here attributed essentially to the H atom in its normal state (cf. I, p. 501, under CH λ3900), while σ is attributed primarily to the other atom.

Additional types. Various additional types also exist, e.g., the triplet type of the second positive nitrogen and Swan (probably C_2) bands (cf. above, p. 1208). These apparently require for their interpretation the assumption of a variable σ and ρ, like the OH bands of Type VII.

Some general results from Table II. From Table II it will be seen that in P and D states, j_e appears essentially as σ in all cases yet known, while in S states it appears in known cases as $\pm\ \epsilon$ (with $\epsilon=0$ for ^1S states). This rule is intimately related to recent theoretical work of Hund (cf. later paper).

A corollary of the empirical rule that S states are of the ρ type, combined with the specifications of the postulates in regard to j and j_e values, is that for such states the nuclear angular momentum m (expressed in quantum units) has (approximately[43]) *half-integral* values (or integral values, if the j values of the quantum mechanics are adopted, —cf. Introduction); for P and D states this is true only for even molecules and then only asymptotically for j values so large that $m=\sqrt{j^2-\sigma^2}$ approximates j. These results are of obvious importance for the theory of the specific heats of diatomic gases.

In a subsequent paper it will be shown that the interpretations given above are strongly supported by observed intensity relations, which show close agreement with those to be expected from the correspondence principle.

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July 20, 1926.

[43] This qualification is to take account of the usual small deviations of j_e from an exact integer or half-integer (cf. above[4]).

CRITICAL POTENTIALS AND THE HEAT OF DISSOCIATION OF HYDROGEN AS DETERMINED FROM ITS ULTRA-VIOLET BAND SPECTRUM[1]

By Enos E. Witmer*

Abstract

Lyman has found that if a tube containing argon with a trace of hydrogen is excited by an uncondensed discharge, a simple spectrum is obtained that consists of twelve groups of lines of the secondary spectrum in the extreme ultra-violet. The group of shortest wave-length is partly obscured by one of the two extremely intense lines of argon, that correspond to its resonance potentials of 11.57 and 11.78 volts. The present investigation has shown that these groups are *bands*, due to the transitions from a single electronic and vibrational state, A, $n'=a$ to the electronic and vibrational states N, $n''=0$ to 11. These bands are apparently Q branches with perturbations near the origin. The first lines fit the empirical formula

$$\nu=94075-4267\ n''+113.5\ n''^2+\cdots$$

The existance of a definite upper state is due to the argon, which, acting through *limitation of electron velocities* and *collisions of the second kind*, limits the energy that can be imparted to a hydrogen molecule to 11.78 volts. This is just sufficient to raise the molecule from the normal state N, $n=0$ to the excited state A, $n=a$. If $a=0$, the radiation potential for these bands is 11.61 volts, which agrees with the experimental values of the lowest radiation potential of the hydrogen molecule. The data permit the computation of the *heat of dissociation*, D, of the hydrogen molecule. The lower limit of D is 4.10 volts or 94,600 calories per mol, and the upper limit 4.56 volts or 105,200 calories. The probable value is 4.34 volts or 100,100 calories. This is in agreement with the best experimental values.

There is a remarkable parallelism between the atomic and molecular spectra of hydrogen, that seems to indicate that the electronic energy levels in the two cases must be very similar. An attempt was therefore made to introduce *total electronic quantum numbers*, e_t, and to compute the higher *critical potentials* of the hydrogen molecule. To the electronic level N was assigned the value $e_t=1$, and to the level A the value $e_t=2$. The ultra-violet band spectrum is due to the transitions $e_t\geqq 2$ to $e_t=1$, and the visible spectrum to the transitions $e_t\geqq 3$ to $e_t=2$. The higher critical potentials were computed by two methods, first, by use of the Glitscher diagram (in Sommerfeld's Atombau), and, secondly, by use of a Rydberg formula. The remarkable agreement between the values obtained by the two methods seems to indicate that these values have some significance. These values are 13.64, 14.32, 14.64, 14.81 volts, etc., giving an ionization potential of 15.19 volts. Several suggestions are made concerning the discrepancy between this value and the experimental values.

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[1]E. E. Witmer, Phys. Rev. **27**, 513 (Abstract) (1926). Proc. Nat. Acad. Sci. **12**, 238–244 (1926).

The *heat of dissociation of the ionized hydrogen molecule* is also obtained. Using our value of the ionization potential of H_2, its value is 2.69 volts. A suggestion is also made concerning the vibrational quantum numbers of the Fulcher Bands. *Other bands* due to the electronic transition *A* to *N* were also found and assigned vibrational quantum numbers.

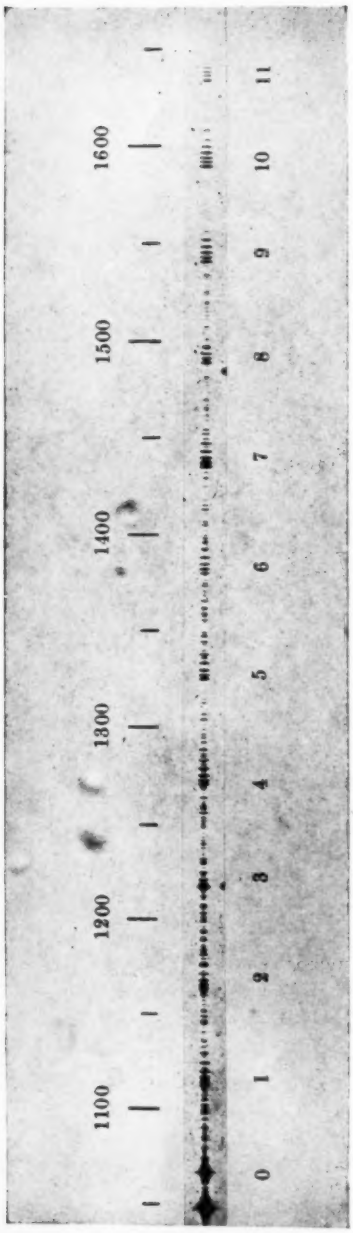

Fig. 1. The Lyman Bands.

THE secondary spectrum of hydrogen is a band spectrum emitted by molecular hydrogen. On account of the small moment of inertia of the hydrogen molecule, however, this spectrum does not have the appearance of an ordinary band spectrum, but rather that of a very rich line spectrum, so that in most cases it is impossible to pick out by mere inspection the lines that belong together in a single band. For this reason it is a very difficult spectrum to analyze without physical methods to assist in determining the correct grouping of the lines. Fortunately it was discovered by Professor Lyman some years ago that under certain conditions of excitation the mixture of small proportions of hydrogen with argon causes the former to emit in the extreme ultra-violet a spectrum very much simpler than the complete secondary spectrum in that region. This spectrum consists of a series of twelve groups of lines. Five of these groups he mentions in his book,[2] "The Spectroscopy of the Extreme Ultra-Violet"; the remaining groups he found on plates taken in May, 1925. The investigation of this spectrum was suggested by Professor Lyman, and the work reported in this paper is based on a study and measurement of his last plates, which were kindly placed at the writer's disposal.

[2]T. Lyman, Spectroscopy of the Extreme Ultra-Violet, pp. 74–81, also Table I in the Appendix.

Fig. 1 is a reproduction of this spectrum with a wave-length scale. The groups have been numbered 0, 1, 2, 3, etc., beginning with the group of shortest wave-length. The zero group is partly obscured by one of the two extremely intense resonance lines of argon, λλ1048.26 and 1066.71, and group 3 is very much fainter than the other groups. The general appearance of the spectrum is that of a one-dimensional series of bands degraded toward the red. The usual second difference test confirms this conclusion. These bands will be referred to hereafter as the Lyman bands.

Practically all the intense lines of this spectrum in the region λλ1230 to 1650 have been identified with lines of the secondary spectrum in Lyman's[2] table. Some of the remaining lines have also been identified on plates of the complete secondary spectrum. Since the numerical relationships show that all the lines belong together, there can be no doubt that the complete spectrum is part of the secondary spectrum.

In measuring these plates the lines of atomic hydrogen have been used as fiducial lines. The first three lines of the Lyman series occur on all these plates, the first two being very intense. In addition to these lines there were available for use as checks the oxygen triplet[3] at λ1302.27, argon lines measured by Professor Saunders, and in one case the third line of the Lyman series in the second order.

In Table I are given the measurements on this spectrum. m denotes the rotational quantum number provisionally assigned to the lines of each band, λ and ν being as usual wave-length in Ångstroms and wave-number respectively. In Band 0 three lines were obscured by the extremely intense argon line λ1066.71, and in Band 3, which is very faint two lines at the head were obscured by the intense line λ1215.68 of atomic hydrogen. The probable values of these missing lines have been inserted in parentheses to complete the table. The wave-lengths given in the table are, with a few exceptions as in the case of faint lines, the average of three or more independent measurements. The greatest deviation from the mean is in every case equal to or less than .20A°.

Assuming the applicability of the well known formula

$$\nu = A + 2Bm + Cm^2 \qquad (1)$$

for the lines of a band, it follows that the second differences should be equal to the constant, $2C$. While there is considerable deviation from constancy in the second differences in Table I, the regularities are sufficient to demonstrate the band character of these groups. Many of the smaller irregularities are probably due to experimental errors in the

[3] J. J. Hopfield and S. W. Leifson, Astrophys. J. **58**, 61 (1923)

wave-lengths; the larger irregularities are real as shown by their constant appearance in all sets of measurements. There is no doubt, for example, that in bands 4–11 inclusive there are irregularities about the head, and that approximately constant second differences are obtained in these cases only if the first two lines be omitted in forming the differences.

TABLE I

The Lyman Bands

m	Intensity	λ	ν	Differences 1st	Differences 2nd
		Band 0			
1	4	1062.98	94 075		
				(47)	
2		(1063.51)	(94 028)		(66)
				(113)	
3		(1064.79)	(93 915)		(83)
				(196)	
4		(1067.02)	(93 719)		(83)
				(279)	
5	5	1070.21	93 440		(83)
				362	
6	4	1074.37	93 078		79
				441	
7	1	1079.48	92 637		
			Ave.	78.8	
		Band 1			
1	8	1112.08	89 922		
				46	
2	8	1112.64	89 876		66
				112	
3	10	1114.03	89 764		75
				187	
4	10	1116.36	89 577		76
				263	
5	9	1119.64	89 314		78
				341	
6	8	1123.94	88 973		68
				409	
7	2	1129.13	88 564		
			Ave.	72.6	
		Band 2			
1	8	1162.88	85 993		
				38	
2	8	1163.40	85 955		71
				109	
3	10	1164.87	85 846		65
				174	
4	10	1167.24	85 672		74
				248	
5	10	1170.63	85 424		66
				314	
6	8	1174.95	85 110		76
				390	
7	1	1180.36	84 720		
			Ave.	70.4	
		Band 3			
1		(1215.02)	(82 303)		
				(45)	
2		(1215.68)	(82 258)		(60)
				(105)	
3	2	1217.24	82 153		(49)
				154	
4	2	1219.52	81 999		82
				236	
5	2	1223.04	81 763		56
				292	
6	0	1227.43	81 471		
			Ave.	61.7	
		Band 4			
1	8	1268.52	78 832		
				24	
2	8	1268.90	78 808		81
				105	
3	10	1270.60	78 703		53
				158	
4	10	1273.15	78 545		57
				215	
5	10	1276.65	78 330		59
				274	
6	8	1281.13	78 056		51
				325	
7	0	1286.49	77 731		
			Ave. (excluding first value)	55.0	
		Band 5			
1	10 *	1322.96	75 588		
				15	
2		1323.22	75 573		
	10 *	1324.64	75 492		
				107	
3		1325.07	75 466		40
				147	
4	10	1327.69	75 319		51
				198	
5	9	1331.18	75 121		54
				252	
6	5	1335.66	74 869		38
				290	
7	0	1340.86	74 579		
			Ave.	45.8	

*These doublets were not resolved sufficiently for accurate measurement.

TABLE I (*Continued*)

The Layman Bands

m	Intensity	λ	ν	Difference 1st	Difference 2nd
		Band 6			
1	6	1377.99	72 569		
				108	
3	7	1380.05	72 461		
				132	
4	8	1382.58	72 329		51
				183	
5	8	1386.07	72 146		43
				226	
6	1	1390.44	71 920		
			Ave.		47.0
		Band 7†			
1	10	1432.83	69 792		
	4	1434.11	69 730	109	
3	10	1435.08	69 683		
	1	1436.11	69 633	121	
4	10	1437.57	69 562		44
				165	
5	10	1440.98	69 397		36
				201	
6	8	1445.18	69 196		40
				241	
7	1	1450.22	68 955		
			Ave.		40.0
		Band 8			
1	5	1486.97	67 251		
				44	
2	0	1487.93	67 207		16
				60	
3	4	1489.26	67 147		47
				107	
4	4	1491.65	67 040		40
				147	
5	3	1494.93	66 893		27
				174	
6	0	1498.82	66 719		
			Ave.		32.5

m	Intensity	λ	ν	Differences 1st	Differences 2nd
		Band 9			
1	6	1539.36	64 962		
				24	
2	1	1539.92	64 938		
				76	
3	6	1541.74	64 862		22
				98	
4	6	1544.07	64 764		28
				126	
5	6	1547.07	64 638		26
				152	
6	2	1550.73	64 486		26
				178	
7	0	1555.01	64 308		
			Ave.		25.5
		Band 10			
1	10	1588.92	62 936		
				48	
2	1	1590.12	62 888		
				49	
3	10	1591.38	62 839		
				82	
4	10	1593.46	62 757		22
				104	
5	10	1596.10	62 653		17
				121	
6	4	1599.19	62 532		23
				144	
7	0	1602.87	62 388		
			Ave.		20.7
		Band 11			
1	3	1633.65	61 213		
				15	
2	3	1634.03	61 198		
				87	
3	4	1636.36	61 111		
				66	
4	4	1638.14	61 045		15
				81	
5	3	1640.32	60 964		13
				94	
6	0	1642.84	60 870		
			Ave.		14.0

The values of C obtained from Table I, though not very accurate, yield the empirical equation

$$C = -(40 - 3p) \qquad (2)$$

where p is the number of the band. This is an extremely large value of C. It shows that there is a very large increase in the moment of inertia of

†There are two lines that by all indications belong to this group, but which do not fit into the scheme.

the hydrogen molecule in going from the lower to the upper of the two electronic states involved in the emission of these bands.

Bands 1 and 2 are apparently Q branches without perturbations. Fig. 2 is a Fortrat diagram of band 1. The remaining bands from 4–11 inclusive can be fitted to parabolic curves in which the second line is usually faint or displaced or both. An example is Fig. 3, which is a diagram of band 11. It will be observed that in this diagram the angle of intersection between the parabola and the ν axis is not quite a right angle, but an acute angle (if one uses the angle in which the parabola lies). This is true of all the bands from 6–11 inclusive and possibly of

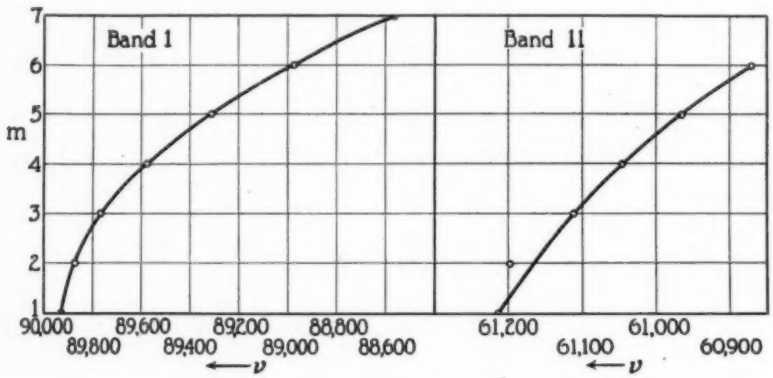

Fig. 2. Fortrat diagram of Lyman band No. 1.
Fig. 3. Fortrat diagram of Lyman band No. 11.

some of the others. If, however, the outer lines 3, 4, 5, etc. of any band be used to compute the constants of the parabola, it is found that the computed head in all cases falls within 20 or 30 cm^{-1} of the first observed line. On the whole these bands fit into the category of Q branches better than any other.

The frequencies of the origin of the bands in any given system are given by the well known formula

$$\nu=\nu_e+n'\omega_0'(1-x'n'+\cdots)-n''\omega_0(1-x''n''+\cdots), \qquad (3)$$

where the primed letters refer to the initial state in emission and the doubly primed letters to the final state,† n being the vibrational quantum number. In this case the frequencies of the first lines of the bands fit the empirical formula

$$\nu=94\ 075-4267p+113.5p^2+\cdots \qquad (4)$$

If these are Q branches, as we suppose, the first line of each band will

†Throughout this paper primed letters refer to the initial state in emission and doubly primed letters to the final state.

lie very close to the origin and we may proceed to identify (3) and (4). Since x in Eq. (3) is positive, almost without exception, it follows that in Eq. (4) the variable part of the left-hand member is a function of n'' rather than n'. For no permissible transformation can change the sign of the coefficient of p^2. This shows that the initial state is constant and the final state variable. It seems highly probable, therefore, that the band of shortest wave-length would have the value $n''=0$, thus making $p=n''$. If in accord with the experimental results of Mulliken[4] and the theoretical results stated by Born and Jordan[5] half-integral vibrational quantum numbers were used, then $n''=p+\frac{1}{2}$. In this paper the integral values will be used for the sake of convenience.

The lower electronic level involved in the emission of these bands will be designated N, and the upper level A.

Mode of Excitation

Lyman[2] describes in detail the conditions under which these bands are emitted to the exclusion of the rest of the secondary spectrum in the extreme ultra-violet. The two essential conditions are that the argon contain only a small proportion of hydrogen and that the discharge be uncondensed. That the argon plays an important rôle is shown, furthermore, by the fact that the head of the zero band lies between the two extremely intense resonance lines of argon, λλ1048.26 and 1066.71. The corresponding resonance potentials are 11.78 and 11.57 volts, while the potential corresponding to the head of the zero band is 11.61 volts. These facts seem to indicate that the lower electronic level N is the normal level of the hydrogen molecule, and that due to the presence of the argon, almost all the excited hydrogen molecules exist in the one electronic and vibrational state A, $n=a$, where a is some definite integer, as yet unknown.

Let us consider in detail the probable conditions in the tube in which these bands are excited. Since the argon is far in excess of the hydrogen, the argon will determine the velocity distribution of the free electrons. The general nature of this distribution must be something like that indicated in Fig. 4. There will be many electrons per volt of velocity below the lowest resonance potential, 11.57 volts, and big drops in the number per volt both at this point and at 11.78 volts. A very large number of the argon atoms will be in these two resonance states.

The hydrogen molecules are initially in the normal electronic state, which will be assumed to be N. The further assumption will be made

[4] R. S. Milliken, Phys. Rev. **25**, 119 (1925).
[5] M. Born and P. Jordan, Zeits. f. Physik. **34**, 858 (1925).

that almost all the hydrogen molecules in this electronic state are in the vibrational state $n=0$. Using the Boltzmann formula, a simple computation shows that even at 1000°K under conditions of thermal equilibrium the number of molecules in the state N, $n=1$ would be only 0.26 percent of the number in the state N, $n=0$; and, while it cannot be assumed that a temperature distribution prevails in a discharge tube, it is at least not unreasonable to suppose that the percentage of molecules in higher vibrational states was in this particular case quite small.

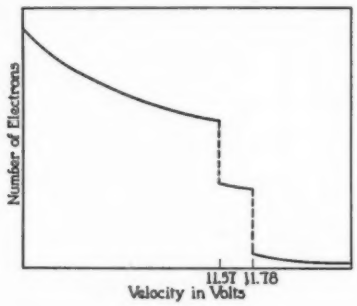

Fig. 4. Diagram showing the probable velocity distribution of the electrons in the discharge tube producing the Lyman bands. 11.57 and 11.78 volts are the resonance potentials of argon.

The hydrogen molecules may be excited by two processes, by collisions of the second kind with argon atoms having an energy of 11.78 volts, and by electron impact. Since the percentage of electrons with velocities greater than 11.78 volts is probably small, it follows that there will be very few hydrogen molecules with an energy greater than this value. This energy is sufficient to raise the hydrogen molecule from the state N, $n=0$ to the state A, $n=a$, an interval of 11.61 volts, but not sufficient to raise it to any higher vibrational or electronic state. Returning to lower levels, all possible transitions occur, namely, A, $n'=a$ to N, $n''=0$ to 11, thereby producing the Lyman bands.

The value of a has not yet been determined. If we may assume that an appreciable percentage of the hydrogen molecules in the state A, $n=a$ have been excited by electron impact, then the states A, $n<a$ will also be excited, and instead of one series of bands there would be $(a+1)$ series. Since only one series is observed this would necessitate making $a=0$. If, however, practically all the molecules in the state A, $n=a$ have been excited by collisions of the second kind, then it is quite evident, that a may have any value in so far as the existence of a single series is concerned. The fact that argon lines of shorter wave-length than λ1048.26 occur on these plates as well as the second and third

lines of the Lyman series proves that there must be a considerable number of electrons with velocities greater than 11.78 volts. The discussion above indicates that the number of electrons per volt of velocity below 11.78 volts is considerably greater than the number per volt above 11.78 volts. One would be inclined to think, therefore, that the percentage of hydrogen molecules excited by electron impact would be appreciable, and that if a is greater than zero, at least faint series would be observed in addition to the Lyman bands. The fact such series were not observed may be considered as evidence in favor of the value $a=0$.

With this value of a the radiation potential for the Lyman bands is 11.61 volts. This is in good agreement with the experimental values[6] of a radiation potential of the hydrogen molecule, which range from 11.5 to 12.0 volts. If a were greater than zero, the value of the radiation potential would be less than 11.61 volts. The value of ω_0 for the electronic state A obtained in the latter part of this paper is 2695 cm^{-1}, which corresponds to .33 volt. From this value, it follows that if a were 1, for example, the radiation potential would be only 11.28 volts, which does not agree with the electron impact experiments as well as the former value.

It is very probable that the radiation potential of 11.61 volts is the lowest one in the hydrogen molecule. For on this theory of excitation, if any part of the secondary spectrum in the extreme ultra-violet had an excitation potential less than this value, one would expect that fact to reveal itself by the presence on these plates of one or more additional series of bands similar to the Lyman bands. Although these plates cover the entire region of the secondary spectrum in the extreme ultra-violet, no other bands were observed. Since the excitation potentials of the visible secondary spectrum[7] range from 13 to 15 volts, it is fairly certain that 11.61 volts is in fact lowest radiation potential. This conclusion is in agreement with the results obtained from electron impact experiments.[6]

Eq. (4) may now be rewritten in terms of the vibrational quantum numbers,

$$\nu = 94\ 075 - (4267n'' - 113.5n''^2 + \cdots). \qquad (5)$$

The value of ω_0, the frequency of infinitesimal vibration for the normal state, obtained from this equation is 4267 cm^{-1} in fair agreement with the value 4880 cm^{-1} obtained by Kemble and Van Vleck[8] from specific heat data.

[6] Bulletin of the National Research Council on Critical Potentials, pp. 114–120.
[7] O. S. Duffendack, Astrophys. J. **60**, 122 (1924).
[8] E. C. Kemble and J. H. Van Vleck, Phys. Rev. **21**, 653 (1923).

Heat of Dissociation

From Eq. (5) it follows that the vibrational energy, E_n, of the hydrogen molecule in the normal electronic state is

$$E_n = h(4267n - 113.5n^2 + \cdots). \tag{6}$$

The frequency of vibration, ω_n, of the nuclei in the vibrational state of quantum number n is

$$\omega_n = \frac{1}{h}\frac{dE_n}{dn} = 4267 - 227.n + \cdots \tag{7}$$

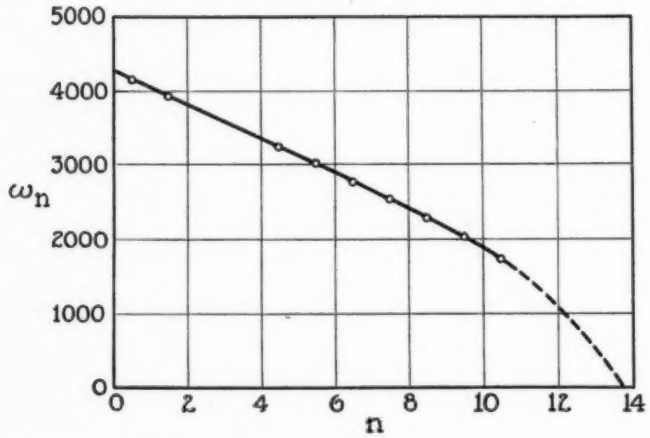

Fig. 5. The frequency of vibration of the nuclei, ω_n, in the normal electronic state of the hydrogen molecule plotted as a function of the vibrational quantum number, n.

Since the higher powers in Eq. (6) are small, dE_n/dn is practically equal to ΔE_n, if the latter be defined as

$$\Delta E_n(n+\tfrac{1}{2}) = E_n(n+1) - E_n(n). \tag{8}$$

The advantage of using the first difference is that its value may be taken directly from the experimental data, as Eq. (8) shows. Fig. 5 is a graph of ω_n or $1/h\,\Delta E_n$ as a function of n. The dotted portion of the curve is an extrapolation. The general nature of this extrapolation is justified both by the trend of the observed part of the curve and by the fact that the hydrogen molecule is homopolar. For the potential energy function of a homopolar molecule, when expressed in descending powers of the internuclear distance r, begins with a power of r equal to or greater than two, and Kratzer[9] has shown that in such cases ω_n becomes zero for a finite value of n.

[9] A. Kratzer, Zeits. f. Physik. **26**, 40 (1924).

According to band spectrum theory the heat of dissociation of a diatomic molecule is $(E_n)_{max}$, the maximum possible vibrational energy in the normal electronic state. As Eq. (7) shows, E_n is a maximum for that value of n at which the frequency of vibration of the nuclei is zero. It follows by integration of Eq. (7) that[10]

$$(E_n)_{max} = h\int_0^{n_0} \omega_n dn \tag{9}$$

where n_0 is the value of n at which $\omega_n = 0$. Stated graphically Eq. (9) means that the area under the curve in Fig. 5 is a measure of $(E_n)_{max}$.

Since the extrapolation in Fig. 5 is more or less uncertain it is best in estimating the value of $(E_n)_{max}$ to get lower and upper limits as well as the probable value. The lower limit was taken as the highest observed value of the combined vibrational and rotational energies, which was obtained by subtracting the energy of the line of longest wave-length in the Lyman bands from that of the shortest wave-length. Its value is 4.10 volts or 94,600 calories per mol. The upper limit was obtained by using as an extrapolation in Fig. 5 a straight line tangent to the curve at the last observed point. Its value is 4.56 volts or 105,200 calories per mol. The probable value corresponds to the extrapolation indicated in Fig. 5. A better way of obtaining the probable value, however, is from an (n, E_n) graph. Its value is 4.34 volts or 100,100 calories per mol. These results are in accord with the best experimental values. Isnardi's result[11] (as corrected by Wohl) is that the heat of dissociation of hydrogen lies between 96,765 and 102,257 calories; while Langmuir's[12] latest value is 97,000 calories.

Critical Potentials

Just as the visible secondary spectrum occurs in the same general region as the Balmer series of atomic hydrogen, so the ultra-violet band spectrum of hydrogen falls in the same general region as the Lyman series. In each case there is a gap[2] between the ultra-violet and visible spectra. According to Franck[13] the visible band spectrum probably holds the same relationship to the ultra-violet band spectrum that the Balmer series does to the Lyman series. The fact that the critical potentials of the visible band spectrum[7] range from 13 to 15 volts makes this con-

[10] Cf. R. T. Birge and H. Sponer, Phys. Rev. **28**, 259 (1926).

[11] T. Isnardi, Zeit. f. Elektrochemie **21**, 405 (1915). K. Wohl (*Ibid.*, **30**, 49, 1924) corrected a slight error in computation in Isnardi's work, thereby raising his value about 5000 calories.

[12] I. Langmuir, G. E. Rev. **29**, 153 (1926).

[13] A. Sommerfeld, Atombau and Spektrallinien, pp. 519–520.

clusion fairly certain. Furthermore, even in the visible there is a close parallel parallelism between the Balmer series and the secondary spectrum. This is shown by the diagram due to Glitscher[14] in the fourth and earlier editions of Sommerfeld's Atombau und Spektrallinien. This diagram is a photometric curve of the secondary spectrum, giving the intensity as a function of the wave number, the resolution being insufficient to show individual lines. Glitscher points out that some of the most prominent peaks on this curve have almost the same spacing as the $\alpha, \beta, \gamma, \delta$ lines of the Balmer series. All these facts seem to indicate that there is a correlation between the electronic energy levels of the hydrogen atom and those of the molecule, and that the spacing of these energy levels is about the same in the two cases. The radiating electron in the molecule, however, is more tightly bound than the electron in the corresponding orbit in the atom. This is shown by the fact that the corresponding potentials of the molecule are always higher. Thus the ionization potential of the molecule is higher than that of the atom, and the lowest resonance potential of the molecule is 11.61 volts, whereas that of the atom is 10.15 volts. Furthermore, on the Glitscher diagram the peaks $\alpha, \beta, \gamma, \delta$ are all on the high frequency side of the corresponding lines of the Balmer series.

These facts seem to justify an attempt to introduce total electronic quantum numbers, e_t, in the sense in which that nomenclature is used in atomic spectra. To the normal electronic level N will be assigned the value $e_t=1$, and to the electronic level A the value $e_t=2$, the difference between these two levels being 11.61 volts. On this theory the ultraviolet band spectrum is due to the transitions $e_t' \geqq 2$ to $e_t''=1$, and the visible band spectrum to the transitions $e_t' \geqq 3$ to $e_t''=2$. For the present it will be assumed that there is only one electronic energy level for each value of e_t, although the reverse is almost certainly the case in reality.

On the basis of this theory an attempt will be made to compute the higher critical potentials of the hydrogen molecule by two methods, first by use of the Glitscher diagram, secondly by use of a Rydberg formula. In the first method the assumption will be made that the peaks marked $\alpha, \beta, \gamma, \delta$ on the Glitscher diagram represent corresponding positions in the band systems due to the transitions $e_t'=3, 4, 5, 6$ respectively to $e_t''=2$. The further assumption will be made that each peak $\alpha, \beta, \gamma, \delta$ represents the location of the (0, 0) band for the electronic transition in question. On these assumptions by adding the voltage corresponding to each of these peaks to 11.61 volts one should obtain

[14]K. Glitscher, Sitzungsber. d. bayer. Akad. p. 125 (1916).

the higher critical potentials and by extrapolation the ionization potential of the hydrogen molecule. This is done in Tables II and III. The values of ν are taken from the Glitscher diagram. The results of this computation are given in the second column of Table III.

In the second method the assumption is made that the critical potentials of the hydrogen molecule follow a Rydberg formula

$$V=13.539\left\{\frac{1}{(1-\alpha)^2}-\frac{1}{(e_t-\alpha)^2}\right\}. \tag{10}$$

This was suggested by the preceding theory, as well as by previous work of Fowler,[15] and Sponer.[16] The value of α was found from the lowest radiation potential by solving the equation

$$11.610=13.539\left\{\frac{1}{(1-\alpha)^2}-\frac{1}{(2-\alpha)^2}\right\}. \tag{11}$$

TABLE II

Peak	ν	$V=1.2344\times10^{-4}\nu$
α	16,650. cm^{-1}	2.055 volts
β	21,850.	2.697
γ	24,500.	3.030
δ	25,900.	3.197

TABLE III

e_t	V	V (calc)
2	11.61 volts	11.610 volts
3	13.665	13.631
4	14.31	14.323
5	14.64	14.639
6	14.81	14.810
∞	15.19	15.193

which gives $\alpha=0.0560$. This value of α was used in Eq. (10) to compute the series of values under V(calc). It will be observed that the agreement between the values obtained by these two independent methods is quite remarkable.

Thus far it has been assumed that to each value of e_t there corresponds only one electronic energy level of the hydrogen molecule. In reality, however, it will probably be found necessary to introduce the azimuthal and inner quantum[17] numbers also in order to classify these energy levels, so that there will be several levels for each value of e_t. Possibly the various levels corresponding to any given value of e_t are close together. That would account for the results given in Table III. In any case a consideration of the remaining electronic quantum numbers will necessitate a reinterpretation of the results in Table III and may possibly alter the numerical values. These considerations may explain the discrepancy between the value of the ionization potential, 15.19 volts,

[15]A. Fowler, Proc. Roy. Soc. **A91,** 208 (1915).
[16]H. Sponer, Zeits. f. Physik. **34,** 622 (1925).
[17]R. T. Birge, Nature, Feb. 1926. R. S. Mulliken, Proc. Nat. Acad. Sci. **12,** 144(1926).

obtained above and the experimental values,[6] which range from 15.6 to 16.7 volts.

On the other hand this discrepancy does not necessarily indicate that one or the other of these values is wrong. For the spectroscopic values of critical potentials represent a difference of electronic energy levels, but the significance of the values obtained from electron impact experiments in the case of molecules is not yet clear. According to recent work of Franck,[18] and also Birge and Sponer,[19] if an electronic transition causes a large change in the moment of inertia of a molecule, then the transition in question, considered as a statistical average at least, cannot occur without exciting a certain minimum of vibrational energy. Where the excitation is by electron impact this additional energy of vibration must come from the impacting electron. Consequently in such cases the observed critical potentials should be higher than the corresponding difference in electronic energy levels.

This type of explanation would probably account for the discrepancy in the case of hydrogen. For, as Eq. (2) shows, there is an extremely large increase in the moment of inertia of the molecule in going from the normal level N to the excited level A. It is reasonable to suppose, therefore, that large changes in the moment of inertia occur when the molecule jumps from the normal electronic level to various higher levels or when ionization occurs. If this is the case, one would expect the observed critical potentials to be higher than the spectroscopic values.

Remarks

If I_a is the ionization potential of the atom of an element, I_m that of its diatomic molecule, D the heat of dissociation of the neutral normal molecule, D' the heat of dissociation of the ionized molecule, it follows from the principle of the conservation of energy that[20]

$$D+I_a=D'+I_m. \tag{12}$$

For hydrogen

$$I_a+D=13.54+4.34=17.88 \text{ volts}$$

If we take $I_m=15.19$ volts

$$D'=2.69 \text{ volts}$$

If we accept the experimental values of I_m, D' will be about 2 volts. Urey's[21] theoretical value is 3.12 volts. Sommerfeld,[22] on the other hand,

[18] J. Franck, Trans. Faraday Soc. **21**, part 3 (1925).
[19] R. T. Birge and H. Sponer, Phys. Rev. **28**, 259 (1926).
[20] Cf. R. T. Birge, Phys. Rev. **27**, 641 (A) (1926).
[21] H. C. Urey, Phys. Rev. **27**, 216 (1926).
[22] A. Sommerfeld, Atombau and Spektrallinien, p. 518.

assumes that $D=I_m-I_a$, which automatically makes $D'=0$. The data from positive ray analysis[23] show that H^+ and H_3^+ appear at the same voltage as H_2^+. At low pressures $(H^++H_3^+)$ forms only a small percentage of the total number of ions, but as the pressure increases the percentage of these ions increases also. This has been interpreted to indicate that the stability of H_2^+ is small or zero. In view of the fact that the energy with which the ions collide after their formation in the apparatus is unknown, this evidence must be considered inconclusive.

It is interesting to note that the First (or Red) Fulcher Band falls under the α peak in the Glitscher diagram. According to Dieke's[24] interpretation each of the so-called Fulcher Bands is a sequence of Q branches. (By a sequence is meant a group of bands for which $\Delta n = n'-n''$ is a constant.) On this interpretation the first line of the band towards the violet[25] in the First Fulcher Band is 16,611 cm^{-1}, whereas the α peak in the Glitscher diagram is 16,650 cm^{-1}. Since the α peak was assumed to represent the location of the (0, 0) band for the electronic jump $e_t'=3$ to $e_t''=2$, this fact suggests that the First Band may be an (n, n) sequence with the (0, 0) band on the violet side. Both the individual bands and the sequence as a whole are then degraded toward the red. If in addition the assumption be made that the Second (or Green) Fulcher Band is an $(n, n-1)$ sequence due to the same electronic jump, the data permit the computation of the value of ω_0 and $x\omega_0$ for the two electronic levels in question. The values obtained are:

For the state $e_t=2$,

$$\omega_0=2589 \text{ cm}^{-1}$$
$$x\omega_0=67.8 \text{ cm}^{-1};$$

For the state $e_t=3$,

$$\omega_0=2303 \text{ cm}^{-1}$$
$$x\omega_0=62.6 \text{ cm}^{-1}.$$

These values are certainly of the right order of magnitude. As evidence of that fact it will be shown that the values of ω_0 and $x\omega_0$ for the state $e_t=2$ give about the correct value for the heat of dissociation, D'', of the hydrogen molecule when in the excited state $e_t=2$. It will be assumed, of course, that in this case the molecule dissociates into one normal atom and one atom in the first excited state, $n=2$. An accurate value of D'' may be obtained from the equation

$$R_a+D=R_m+D'', \tag{13}$$

[23] H. D. Smyth, Phys. Rev. **25**, 452 (1925); T. R. Hogness and E. G. Lunn, *Ibid.* **26**, 44 (1925).

[24] G. H. Dieke, Proc. Roy. Acad. Amsterdam **27**, 490 (1924); Phil. Mag. **50**, 173 (1925).

[25] For a table of these bands see W. E. Curtis, Proc. Roy. Soc. **A107**, 570 (1925).

which is analogous to Eq. (12). Here R_a is the lowest resonance potential of the atom, and R_m that of the molecule. Inserting the values of the known quantities

$$D''=10.15-11.61+4.34$$
$$=2.88 \text{ volts}$$

If for the electronic state $e_i=2$, the vibrational energy is

$$E_n=h(2589n-67.8n^2), \tag{14}$$

the maximum value of E_n is 3.05 volts. This is a little higher than the preceding value—a result one would expect, considering the fact that the higher powers in Eq. (14) were omitted. One should remember also that the first value applies to the upper electronic state A of the Lyman bands, and the second to the lower state of Fulcher Bands, and that these two states may not be the same.

Other Bands

From Lyman's plates of the complete secondary spectrum in the extreme ultra-violet it was found that by mere inspection one could pick out groups of lines that resembled the Lyman bands. Measurements were therefore made of the lines in these groups and the usual numerical and graphical tests for bands applied. In this way some bands were found whose genuineness seemed fairly certain. Numerical relationships were found between eight of these bands and the Lyman bands, which showed that these eight bands certainly had the same final electronic state as the Lyman bands, and most probably the same initial electronic state. These relationships made possible the assignment of the vibrational quantum numbers. These bands are given in Table IV.

The value of the vibrational energy function for the electronic state A obtained from these bands is

$$E_n=h(2695n-77n^2+\cdots). \tag{15}$$

The values of the constants here are almost the same as the values in Eq. (14) for the final state of the Fulcher Bands.

The correctness of the assignment of the values of the quantum numbers may be tested by the combination relation

$$Q(n_1',n_1'',m)-Q(n_1',n_2'',m)=$$
$$Q(n_2',n_1'',m)-Q(n_2',n_2'',m)=$$
$$F(n_2'',m)-F(n_1'',m), \tag{16}$$

where F is the term function for the final electronic state. The differences

TABLE IV

Additional bands of hydrogen.

m	Intensity	λ	ν	Differences 1st	Differences 2nd
		Band A ($n'=2$, $n''=1$)			
1	8	1052.63	95 000		
				127	
3	8	1054.04	94 873		
				104	
4	7	1055.20	94 769		41
				147	
5	8	1056.84	94 622		37
				184	
6	9	1058.90	94 438		
		Band B ($n'=2$, $n''=2$)			
1	6	1098.01	91 074		
				113	
3	6	1099.37	90 961		
				97	
4	5	1100.54	90 864		31
				128	
5	6	1102.10	90 736		66
				194	
6	6	1104.46	90 542		26
				220	
7	6	1107.15	90 322		48
				268	
8	4	1110.45	90 054		
		Band C ($n'=2$, $n''=3$)			
1	8	1144.34	87 387		
				122	
3	8	1145.93	87 265		
				76	
4	5	1146.94	87 189		48
				124	
5	7	1148.57	87 065		48
				172	
6	7	1150.84	86 893		
		Band D ($n'=3$, $n''=3$)			
1	7	1115.06	89 681		
				103	
3	7	†1116.34	89 578		
				88	
4	3	1117.44	89 490		39
				127	
5	8	1119.03	89 363		45
				172	
6	7	1121.19	89 191		38
				210	
7	5	†1123.84	88 981		57
				267	
8	3	1127.22	88 714		
		Band E ($n'=3$, $n''=4$)			
1	10	1159.76	86 225		
				115	
3	9	1161.31	86 110		
				75	
4	5	1162.32	86 035		33
				108	
5	9	1163.78	85 927		61
				169	
6	8	1166.07	85 758		
		Band F ($n'=3$, $n''=5$)			
1	6	1205.07	82 983		
				107	
3	6	1206.62	82 876		
				64	
4	3	1207.55	82 812		32
				96	
5	4	1208.95	82 716		
		Band G ($n'=4$, $n''=2$)			
1	4	1046.60	95 547		
				114	
3	5	1047.86	95 433		
				103	
4	3	1048.99	95 330		51
				154	
5	4	1050.68	95 176		12
				166	
6	4	*1052.52	95 010		
		Band H ($n'=4$, $n''=5$)			
1	8	1174.32	85 156		
				108	
3	8	1175.80	85 048		
				63	
4	4	1176.68	84 985		47
				110	
5	8	1178.21	84 875		55
				165	
6	7	†1180.50	84 710		
		Band I			
1	4	953.53	104 873		
				120	
3	5	954.63	104 753		
				106	
4	4	955.59	104 647		30
				136	
5	4	956.84	104 511		37
				173	
6	2	958.42	104 338		

†Apparently coincides with a line of the Lyman bands.
*Apparently coincides with a line of Band A.

obtained from these bands and the Lyman bands are given in Table V.

While some of the individual lines in the bands in Table IV may be incorrect, the process by which they were picked out as well as the numerical relationships would seem to indicate that on the whole they are genuine.

TABLE V

m	Band 1–Band 2	Band A–Band B	m	Band 4–Band 5	Band E–Band F
1	3929	3926	1	3244	3242
2	3921	———	2	3235	———
3	3918	3912	3	3237	3234
4	3905	3905	4	3226	3223
5	3890	3886	5	3209	3211
6	3863	3896			

m	Band 2–Band 3	Band B–Band C	m	Band 2–Band 5	Band G–Band H
1	(3690)	3687	1	10405	10 391
2	(3697)	———	2	10382	———
3	3693	3696	3	10380	10 385
4	3673	3675	4	10353	10 345
5	3661	3671	5	10303	10 301
6	3639	3649	6	10241	10 300

m	Band 3–Band 4	Band D–Band E
1	3471	3456
2	3450	———
3	3450	3468
4	3454	3455
5	3433	3436
6	3415	3433

The writer wishes to express his thanks to Professor T. Lyman, who obtained the spectrum plates used in this investigation, and to Professor E. C. Kemble and Dr. R. S. Mulliken, whose criticism and suggestions have been of great value.

JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY,
August 18, 1926.

Note added in proof. While the spectroscopic data given in this paper are insufficient to determine a (the value of n' for the upper electronic state A of the Lyman Bands), a consideration of the process of excitation and the experimental values of the lowest radiation potential of H_2 led us to the probably conclusion that $a=0$. G. H. Dieke and J. J. Hopfield have recently shown, however, (private communication) from their admirable analysis of the absorption spectrum of the hydrogen molecule that this conclusion is incorrect and that $a=3$. This, of course, alters the value of the lowest radiation potential. Their value is 11.1 volts. They also find a third electronic level at 12.2 volts above the normal

level N. Designating this level as B, the *other bands* in this paper are due, according to their analysis, to the electronic transition $B \rightarrow N$. It might seem that these changes would entirely invalidate the results given in Table III. Such is not the case, however. For, using the terminology above, it seems probable that both the electronic level A at 11.1 volts and B at 12.2 volts have the value $e_t = 2$. The upper of these two orbits is evidently more hydrogen-like, and is therefore the better one to use in computing the probable values of the higher critical potentials. Using 12.2 everywhere instead of 11.61 volts in computing the values of V and V (calc) in Table III, one obtains the results given in Table IIIa.

TABLE IIIa

e_t:	2	3	4	5	6	∞
V:	12.20	14.26	14.90	15.23	15.40	15.78
V (calc):	12.20	14.275	14.98	15.30	15.47	15.86

The value of α used in computing V (calc) from Eq. (10) was $\alpha = 0.0760$. The agreement between V and V (calc), though not as good as in Table III, is still fair, and, what is perhaps more significant, the resulting value of the ionization potential is in good agreement with the best experimental values. In accordance with our previous statements the values in Table IIIa should not be regarded, strictly speaking, as the only higher critical potentials of H_2, but rather as one of several Rydberg or Ritz series.

ON THE ELECTRICAL DISCHARGE IN MIXED GASES

By F. Richard Terroux

Abstract

Spectra of argon, hydrogen and oxygen in the negative glow and positive column of a discharge tube containing A – H_2 and A – O_2 mixtures.—The following mixtures were used: (1) H_2 90% – A 10%, (2) H_2 50% – A 50%, (3) O_2 90% – A 10%, (4) O_2 50% – A 50%. Tables are given showing the principal lines in each region, and their estimated relative intensities. In all four cases the change in concentration was found to make little difference in the distribution of electronic energy. In (1) the argon red spectrum is very strongly excited in the positive column and the blue spectrum appears most intensely in the negative glow. A considerable number of electrons in the positive column possess energies of about 16 volts, while their energy in the negative glow reaches as much as 38 and 40 volts. In (3) and (4) the electrons on the whole possess energies of a higher order in both regions. The argon blue spectrum, the hydrogen Balmer series, and the oxygen series and elementary spectra predominate in the negative glow, whereas the argon red spectrum is most intense in the positive column. The behavior of the Balmer lines in hydrogen and argon is the opposite of its behavior in hydrogen and helium. The *striated state* was produced in every mixture, and abrupt changes in the discharge occurred, when the pressure was reduced to critical values. *The rotation of inclined striae* is connected with the intermittency of the discharge.

Introduction

An examination of the spectra emitted by different regions of the discharge, in mixtures of hydrogen and nitrogen and of hydrogen and helium was recently carried out by Keys and Home.[1] The present paper deals with a similar investigation in mixtures of argon and hydrogen, and of argon and oxygen. Different proportions of the gases were tried and their effect was recorded.

The spectrographic examination of the discharge possesses the following advantages; (1) it introduces no foreign element into the discharge, (2) it is applicable to any region of any type of discharge with equal facility, and (3) it provides data whereby the average energy of the moving electrons and the states of excitation of the atoms and molecules may be determined. This method is only limited by our power to interpret the spectra in terms of atomic states and energy distributions, whether electronic or quantum.

This method is not of recent inspiration, for De La Rue and Müller[2] found some fifty years ago, that in hydrogen, the Balmer lines were more strongly excited in the negative glow than elsewhere. The same discharge

[1] Keys and Home, Phys. Rev. **27**, 709 (1926).
[2] De La Rue and Müller, Phil. Trans. **178**, 155 (1878).

was examined by Crookes[3] who proved that the bluish sheath occasionally found on the convex side of striae was due to mercury vapour. More recently we have the work of Whiddington[4] on hydrogen and argon, and of Banerji[5] on argon. The spectrum of the mercury vapour and hydrogen discharge has been studied by Turner and Compton,[6] and of the striated hydrogen discharge by Keys.[7]

In the present work the spectra of the negative glow and of the striated positive column were obtained and interpreted as far as possible.

Apparatus

The discharge tube was of quartz; 2.3 cm in diameter and 90 cm long, fitted with aluminium disc electrodes, 2.2 cm in diameter, placed 62 cm apart. One of the electrodes was water cooled. A Cenco "Hyvac" pump and a charcoal bulb in liquid air were used in exhausting the tube, which was excited by the direct current from a 300–6000 volt motor generator by Evershed. The spectra were obtained with a Hilger E2 quartz spectrograph, and in addition a constant deviation glass spectrograph was frequently employed. The iron arc was used for comparison purposes. The gases were mixed and carefully dried before being admitted to the tube, which was washed thoroughly before an exposure was attempted. Wratten and Wainwright, and Ilford Rapid Process, Panchromatic plates were used throughout.

Observations

The conditions under which the four principal plates were obtained are shown in Table I.

Table I

No.	Mixture	Pressure	Current	Potential	Exposure	Plate
I	A 90%–H 10%	.18 mm	8 m. a.	1100 volts	6 hrs.	Ilf.
II	A 50%–H 50%	.09 mm	4 m. a.	1500 volts	3.7 hrs.	W & W.
III	A 10%–O 90%	.01 mm	1 m. a.	1800 volts	4.5 hrs.	W & W.
IV	A 50%–O 50%	.07 mm	2 m. a.	1500 volts	7 hrs.	Ilf.

Only the principal lines on these plates were considered and they are given in the following Tables II, III, IV. The columns under N.g. and P.c. give the estimated relative intensities of the lines in the negative glow and positive column respectively.

[3]Crookes, Proc. Roy. Soc. **69,** 399 (1902).
[4]Whiddington, Nature **116,** 506 (1925).
[5]Banerji, Nature **116,** 429 (1925).
[6]Turner and Compton, Phys. Rev. **25,** 606 (1925).
[7]Keys, Trans. R. S. C. **19,** 143 (1925).

TABLE II

The spectrum of argon in the negative glow and positive column of a discharge tube. Plate I = *A* 90%–H_2 10%. Plate III = *A* 10%–O_2 90%. Plate IV = 50%–O^2 50%

Wave-length	Plate I. N.	I. g/P. c	III. N.	III. g/P. c	IV. N.	IV. g/P. c
	Blue spectrum					
4848	3	0				
4765			3	1		
4727			5	1		
4675	7	0				
4658			3	1		
4610	8	0	3	1	3	0
4590	7	0				
4579	7	0				
4545	8	0				
4491			1	1		
4482	6	0			1	0
4432	5	0				
4426	6	0			1	0
4401	5	0			2	0
4379	5	0				
4371					3	0
4348	7	1				
4331	7	0				
4283					9	0
4277	9	0	8	4		
4237	5	0	6	0		
4223	3	0				
4156			2	2	4	4
4132	9	0	2	0	3	0
4113			2	0		
4104	5	0				
4082	4	0				
4073	8	0	3	0	3	0
4053	6	0	2	0	3	0
4043	7	0			3	0
4014	3	0				
3996	4	0				
3968	3	0	3	0		
3961					4	0
3944					3	0
3919	10	0				
3915					9	0
3908			3	2		
3851	6	0	3	0		
3803	7	0	7	9		
3754			7	9	6	1
3729	7	0				
3582	7	0	6	1		
3577	8	1	7	10	10	9
3560	6	0				
3546	9	0	2	0		
3535	6	1	6	1	8	8
3509	6	0	2	0		
3491	9	0				
3392			2	0		
3286			5	4		
3282					4	4
3264			4	1	2	3
3093	8	0	5	0	6	1

Wave-length	Plate I. N.	I. g/P. c	III. N.	III. g/P. c	IV. N.	IV. g/P. c
3034			2	0	1	0
2979	8	0			4	0
2943	10	0	4	0	7	2
2879					6	1
2754	7	0			3	0
2708	2	0			1	0
2479			4	2		
2439			4	3		
2421					3	0
2338					3	0
	Red spectrum					
6416	1	6				
6032	0	5				
6026			1	1		
5912	1	4				
5607	1	4				
5559	1	4				
5506	0	2				
5496	1	4				
5452	1	3				
5253	1	3				
5222	1	3				
5163	1	4				
4868	1	4				
4629	1	4				
4596	1	4				
4522	0	4				
4511	4	10	3	4	2	5
4345	2	6	3	5		
4335	0	9	3	4	0	4
4300	3	10				
4272	3	10	1	4		
4266	2	8				
4259	5	10			5	6
4201	5	10	4	7	6	6
4198	3	10				
4182	3	9				
4164	3	8				
4159	5	10			4	6
4044	3	10			3	6
3949	3	9	3	6		
3894					0	3
3835	2	6				
3670	0	3	2	3		
3650	0	8				
3635	1	5				
3554	0	5				
3460	0	3				
3374	7	8			9	10
3305			2	5		
3022	0	2				
2967	0	2			0	3
2834	0	1				
2802					0	1

Discussion

Plate I. Argon 90 percent—Hydrogen 10 percent. In the positive column we find the argon red spectrum very strongly developed, whereas in the negative glow it is comparatively weak. On the other hand the blue spectrum, which is intense in the negative glow, is represented by three feeble lines in the positive column. The primary hydrogen spectrum is quite strong in the negative glow, and weak in the positive column. The secondary hydrogen spectrum is distributed with more impartiality in both regions.

Table III

The spectrum of hydrogen in the negative glow and positive column of a discharge tube.
Plate I = *A* 90%–H_2 10%. Plate II = *A* 50%–H_2 50%

Hydrogen primary spectrum Wave-length	Plate I. N.	I. P.c	Plate II. N.	II. P.c	Hydrogen secondary spectrum Wave-length	Plate I N.	I. P.c
6563 Hα	10	4	10	1	6299	0	3
4861 Hβ	7	2	8	1	6135	1	3
					5888	0	4
					5505	0	3
4340 Hγ	6	1	6	1	4474	5	0
					4171	1	1
4101	7	1	5	0	4070	1	1
3970	2	1	3	0	4063	0	3
3835	5	4	3	0	3998	5	5
3791	1	1	0	0	3993	2	1
3771	1	1	0	0	3990	3	1
3712	1	1	0	0	3872	1	1
					3805	5	6
					3797	1	1
					3684	1	0
					3674	1	1

From the work of Dejardin,[8] Horton and Davies,[9] Shaver,[10] and Barton,[11] it appears that the argon atom is ionised at about 15.2 volts, and furthermore that at this potential the whole red spectrum is emitted. It is evident therefore, that a large number of argon ions are present in the positive column, and that the "velocity" of a great number of electrons in this region is close to 15.2 volts. Were it less, the red spectrum could not be so intense. On the other hand, the comparative weakness of the Balmer lines; which, according to Horton and Davies,[12] Smyth,[13] and Duffendack,[14] correspond to a potential of about 16 volts, indicates that it can hardly be in excess of the above value.

[8]Dejardin, C. R. **172**, 1482 (1921); Ann. d. Physique **10**, 241 (1924).
[9]Horton and Davies, Proc. Roy. Soc. **97**, 1 (1920) and **102**, 131 (1922).
[10]Shaver, Trans. R. S. C. **16**, 135 (1922).
[11]Barton, Phys. Rev. **25**, 469 (1925).
[12]Horton and Davies, Phil. Mag. **46**, 872 (1923).
[13]Smyth, Phys. Rev. **25**, 452 (1925).
[14]Duffendack, Phys. Rev. **20**, 665 (1922).

The relative weakness of the red spectrum in the negative glow is perhaps due to the average energy of the electrons being greatly in excess of the first ionising potential. The great intensity of the blue lines requires potentials of a much higher order.

A number of authorities are of the opinion that at 34 volts, when the blue spectrum appears, the argon atom is doubly ionised. (At high

TABLE IV

The spectrum of oxygen in the negative glow and positive column of a discharge ube. Plate III = *A* 10%–O_2 90%. Plate IV = *A* 50%–O_2 50%.

Oxygen "series" spectrum					Oxygen "elementary" line spectrum				
Wave-length	Plate III. N.	g/P.	Plate IV. N.	g/P.	Wave-length	Plate III. N.	g/P.	Plate IV. N.	g/P.
1*S*–*mP*					4662	4	1		
4368 (2)	3	1	3	0	4609	3	0	3	0
3692 (3)	3	0			4590			3	0
1*s*–*mp*					4415	4	3		
3947 (2)	3	6	3	0	4369			3	0
1*p*–*ms*					4367	3	1		
4674 (7)	4	0			4345	3	4		
4588 (8)	3	0			4337	3	3	4	4
1*p*–*md*					4276	8	4		
4773 (6)	1	0			4156	2	3	4	5
4654 (7)	3	1	2	0	4154	2	0		
4233	6	0	3	0	4143	2	2		
2897	9	3	6	1	4122	2	0		
2895	9	3	6	1	4114	2	0		
2884	9	3	6	1	4070			3	0
2882	9	3	6	1	4060	4	7	3	0
2753			3	0	3998	4	7	5	6
2708			1	0	3962	3	0	4	0
2474	3	1			3952	3	0		
2446	4	3			3912	10	5	4	4
2420	3	0			3907	3	2		
2325	3	0			3896	3	2	0	3
2299	3	0			3883	3	2	5	0
					3805	7	9	7	8
					3755	7	9	6	7
					3712	4	7	5	6
					3390	2	0		
					3135	6	8	7	8

current densities, a 19 volt impact, doubtless with an ion, will produce the 34 volt blue spectrum; thus 15+19=34 volts.) In their experiments, Lowe and Rose,[15] were unable to produce any blue lines below 39 volts, and Barton,[11] by positive ray analysis found no double ions below 45 volts. Stark[16] classifies a number of lines of the blue spectrum as "bivalent" or "trivalent," and associates these with the formation of double or triple ions respectively. Horton and Davies[9] accept the formation of double ions at 34 volts, and in their 1922 paper give tables showing

[15]Lowe and Rose, Trans. R. S. C. **18,** 313 (1924).

[16]Stark, Ann. d. Physik. **42,** 241 (1913).

the electron energies (in volts) necessary to excite a number of blue lines, as well as the variation of intensity with voltage. Using these data, which appear reliable, we can form an estimate of electron energies in the negative glow. The occurrence, as well as the intensity, of the blue lines in this region (cf Table II) points to the presence of electrons having "velocities" of as high as 38 and 42 volts. A number of double argon ions are doubtless formed in this region. It is known that line intensity depends also upon other factors, such as current density and the presence of other gases. The strong excitation of the Balmer lines may result from 29.4 volt collisions which, according to Horton and Davies,[12] can dissociate the hydrogen molecule and ionise both atoms.

Plate II. Argon 50 percent—Hydrogen 50 percent. The argon spectra on this plate were distributed in exactly the same manner, and point to the same distribution of energy as in the last plate. True, the number of argon lines is somewhat less, but this may be accounted for by the smaller number of argon atoms present. Even though more hydrogen was present in this case, the Balmer lines are both fewer and weaker than in the preceding case. This may be accounted for in two ways: first, that the velocity of most electrons in the positive column was lower than in the previous case, or second, that the Balmer lines were enhanced in the previous case by the presence of a great excess of argon atoms. Indeed both causes may have co-existed. In the negative glow, the Balmer lines are as intense but no more so than in the first Plate.

Spectra taken of both sides of striae in this mixture show only this difference, that the lines are more intense on the cathode side, indicating an excess of excited atoms on this surface, as is to be expected. It was also found that the spectra of striae were more intense than of the uniform positive column in the same mixture.

Plate III. Argon 10 percent—Oxygen 90 percent. With regard to the argon spectrum, two facts are to be noted; First, that much fewer lines are present than in Plates I and II, and second, that the contrast between the lines in the two regions is less marked. The scarcity of lines is attributed to the small proportion of argon atoms present.

In this case, the pressure is low, the potential across the tube high and the current small. We should therefore expect higher electron energies in both regions. A number of blue lines is found in the positive column, which may arise from electron collisions with single ions. The "velocity" of a number of electrons is therefore at least 19 volts and perhaps as high as 34 volts. Radiation may also play an hitherto undetermined part. Not only are there many single argon ions formed in the positive column, but also some double ions.

In the negative glow however, the blue lines present are of such an intensity that they point to electronic velocities of over 42 volts, and it seems certain that double ions are formed by single electron impacts. Thus it seems that in this region also, the average electronic energy is rather greater than in cases I and II.

The oxygen "series" spectrum is strong in the negative glow, and less so in the positive column. The notation in Table IV is Fowler's. Two striking pairs of lines; 2897–5 and 2884–2 are found in the ultra-violet. The resonance and ionisation potentials are given by Foote and Mohler,[17] as 7.9 and 15.5 volts respectively, and further, the second and third ionisation potentials of 32 and 50 volts are given by Payne.[18] According to Fowler,[19] the series spectrum is due to the neutral oxygen atom, and this is excited by collision of 15.5 volts. To dissociate the molecule and ionise an atom requires, according to Hogness and Lunn,[20] a velocity of 20 volts.

Though the oxygen atom may be ionised by a 15.5 volt collision, the dissociation of the molecule by a 7.5 volt collision has not been observed. The greater excitation in the negative glow is attributed to the greater proportion of electrons having energies of 20 volts in that region.

The elementary spectrum is due, according to Fowler,[19] to ionised oxygen, and the calculated potential for excitation is 29.5 volts, which is in close accord to the value given by Payne.[18] This spectrum is more strongly developed in the negative glow, as is to be expected, and where it occurs in the positive column may be attributed to a cumulative process.

Plate IV. Argon 50 percent—Oxygen 50 percent. In this Plate the argon spectrum is naturally stronger than in Plate III. From the distribution of the red and blue spectra, it appears that the average electronic energy in the negative glow is about 38 volts, and that in the positive column the majority of electrons have energies of about 16 volts. The oxygen spectrum occurs in the same manner as before, but the number of lines is diminished by the smaller proportion of oxygen present. It is evident that until more has been done, co-relating the exciting potentials and the spectra emitted, it will be very difficult accurately to interpret all the data available.

In the discharge in hydrogen and helium, Keys and Home[1] found the Balmer lines more strongly developed in the striation than in the

[17]Foote and Mohler, Bull. Bur. Stand. **16**, 669 (1920).
[18]Miss Payne, "Stellar Atmospheres". Harvard (1925).
[19]Fowler, Proc. Roy. Soc. **110**, 476 (1926).
[20]Hogness and Lunn, Phys. Rev. **27**, 732 (1926).

negative glow, whereas the reverse appears in hydrogen and argon. This may be due to the fact that in argon and hydrogen the ionisation potential of argon is but slightly less than that of hydrogen, whereas that of helium is one and a half times as great. An electron having a velocity of a little over 15 volts would probably make an elastic collision with a helium atom, and could still ionise a hydrogen atom; but the same electron colliding with an argon atom would ionise the latter and lose its kinetic energy. Thus in Plates I and II the red argon spectrum was very intense and the hydrogen primary spectrum weak. A further number of mixtures must be tried under different conditions to form a basis for a general theory.

Observations on Striae

1. Striae were produced in every mixture tried, and in some cases remained steady for several hours.

2. As the pressure was gradually diminished, a critical value was reached at which a group of from three to ten striae suddenly disappeared from the negative end of the positive column. This group reappeared again several times, but if the pressure still diminished, finally vanished completely. The process was reversed by increasing the pressure. Every time such a group was dropped, the current fell to about one quarter of its original value.

3. Inclined striae occurred when the tube had not been used for several days, and these could be set in rapid rotation by a uniform magnetic field. *Spontaneous rotation of striae*, due presumably to the earth's field, was noticed in helium and oxygen. The rotation of a column is a periodic phenomenon, and must be connected with a periodic cause. The current, even when a direct source was used, has been found to be periodically intermittent in the discharge, as proved by the rotating mirror, the telephone receiver and the cathode-ray oscillograph, and this must be considered in any explanation of the rotation. The inclination of striae is attributed to initial unequal charges on the walls of the tube which may deviate the streams of ions in the discharge. The inclination disappears in about half an hour, doubtless when the wall charges have become equalized by the ions.

The writer is indebted to the National Research Council of Canada for a bursary, during the tenure of which this work was carried on, and to Dr. D. A. Keys of this Department for suggesting the problem and for his constant interest and advice.

The Macdonald Physics Building,
McGill University,
July 7, 1926.

DETERMINATION OF ELECTRONIC CHARGE FROM MEASUREMENTS OF SHOT-EFFECT IN APERIODIC CIRCUITS

By N. H. Williams and H. B. Vincent

Abstract

An outstanding difficulty in the measurement of electronic charge from shot-effect in a tuned circuit has been regeneration into this circuit. Former methods of dealing with that feature have added tedious computations to Schottky's original calculation. The solution presented here yields the result in such a form that much of the labor is eliminated; the solution is of great mathematical simplicity, and measurement of high-frequency resistance and resonance frequency becomes unnecessary. The treatment may be generalized to include the non-resonant case if the assumption be made that the resonance curve of the amplifier is symmetrical.

A non-inductive resistance may be used as the medium of coupling, and experimental work with this system yields the mean result for electronic charge of 4.774×10^{10} e.s.u.

In work under conditions other than those of temperature limitation, the diminution of fluctuations seems to be due to high current densities rather than space charge in the region of the filament.

Introduction

IF THE emission of electrons from the hot cathode of a vacuum tube is a random process, probability fluctuations of anode current are to be expected. In 1918, Schottky[1] derived an expression for the root mean square voltage one might expect to exist between the terminals when a temperature-limited thermionic current is caused to flow through a tuned circuit. This expression involves certain constants of the circuit, the current, and the magnitude of the electronic charge, ϵ; thus a measurement of the r.m.s. voltage, the current and the other factors involved, yields a measure, by purely electrical methods, of the value of ϵ.

Fürth,[2] Ornstein and Burger,[3] and Fry[4] have arrived at the same theoretical results by a variety of methods, while experimental work has been done by Hartmann,[5] Hull and Williams,[6] and Johnson.[7] Of these latter, the results of Hull and Williams are in agreement with the

[1] W. Schottky, Ann. d. Physik **57**, 541-67 (1918); **68**, 157-76 (1922).
[2] R. Fürth, Phys. Zeits. **23**, 354 (1922).
[3] L. S. Ornstein and H. C. Burger, Ann. d. Physik **70**, 622 (1923).
[4] T. C. Fry, J. of Franklin Inst. **00**, 199 (1925).
[5] C. A. Hartmann, Ann. d. Physik **65**, 51 (1921).
[6] A. W. Hull and N. H. Williams, Phys. Rev. **25**, 147 (1925).
[7] J. B. Johnson, Phys. Rev. **26**, 71 (1925).

theory,—the others, working at much lower frequencies, have failed to realize the expected magnitudes.

Schottky developed the thermionic current ι into a Fourier series,

$$\iota = \Sigma C_k \sin(\omega_k t + \phi_k)$$

and proceeded to determine the mean energy produced. If, however, use is made of an amplifier of the tuned-circuit type, each component of the series is amplified by a different amount, and this must be taken into account in the computations. The adaptations made by Hull and Williams to render the discussion applicable to the case where the voltage across the condenser of the tuned circuit is applied to an amplifier of this type, yields for the mean square output voltage of the amplifier

$$\overline{E^2} = A_0^2 L \iota_0 \epsilon F / 2C^2 R \cdot$$

A_0 is the voltage amplification at the resonance frequency; L is the self-inductance; C, the capacity, and R, the resistance of the tuned circuit, R to include losses in condenser and vacuum tube; ι_0 is the average thermionic current as read by a D.C. ammeter; ϵ is the electronic charge, and F is a factor which is obtained from the resonance curve, $f(x)$, of the amplifier, where $x = \omega/\omega_0$, ω_0 being 2π times the resonance frequency of both the amplifier and the tuned circuit. It is the mean square voltage output divided by the output that would be experienced if all components were subject to the same voltage amplification, A_0.

If the shot-voltage be disconnected and a sine wave of frequency $\omega_0/2\pi$ and r.m.s. voltage v_1 be applied to the amplifier, the output r.m.s. voltage will be $A_0 v_1$. If this produces the same mean square effect as the shot-voltage, we have $\overline{E^2} = A_0^2 v_1^2 = A_0^2 L \iota_0 \epsilon F / 2C^2 R$ or $v_1^2 = L \iota_0 \epsilon F / 2C^2 R$ whence $\epsilon = 2C^2 R v_1^2 / L \iota_0 F$.

Difficulties Attending Regeneration

This substitution method will yield correct results only if regeneration effects are absent. This condition was realized by Hull and Williams in their first work on these measurements, but with larger values of A_0 there are good grounds for believing that regeneration is unavoidable. That is, energy from the output of some or all of the tubes is fed back into the initial circuit where the shot-effect is generated. An ingenious method of procedure enables one to take account of feed-back. If the sine voltage v_1 be introduced into the tuned circuit as shown in Fig. 1 the resonance curve of the system, $f(x)$, may be obtained by the application of voltage of different frequencies. This will give a measure of the amplification with regeneration. If v_1 be applied to the system by the

potential drop across a small impedance L_1 of negligible resistance, carrying a known high-frequency current I_1, the circuit is capable of development of shot-effect with the same efficiency as before. In this case one uses either the vacuum tube $V\,T$ to produce a thermionic current and shot-effect, or, cutting off the filament current, causes I_1 to flow through L_1 to produce the voltage v_1 for calibration or comparison. The tuned circuit is never disconnected nor detuned and regeneration causes no difficulty since it produces the same effect in both $f(x)$ and subsequent measurements.

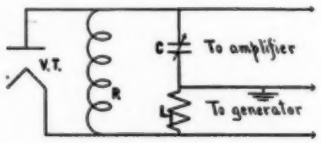

Fig. 1. Diagram showing method of introduction of calibrating voltage into shot-circuit.

Inconvenience is experienced however with this curve, $f(x)$. What one wishes to know is not how a voltage introduced into the circuit, but rather the voltage across the condenser, is amplified.

If v_{oc} is the condenser voltage at the frequency $\omega_0/2\pi$, and v_{kc} at $\omega_k/2\pi$, then with I_1 held constant

$$v_{0c}/v_{kc}=\sqrt{\omega_k^2+(L^2/R^2)(\omega_k^2-\omega_0^2)^2}/\omega_k$$

If $\phi(x)$ be the curve obtained by plotting relative power output against x, and $f(x)$ the curve that would be obtained were the condenser voltage maintained constant, we have

$$\phi(x)=E_k^2/E_0^2=A_0^2 vkc^2 f(x)/A_0^2 v_{0c}^2$$

and

$$f(x)=\phi(x)v_{0c}^2/v_{kc}^2$$

That is, each ordinate of the experimentally determined curve $\phi(x)$ must be multiplied by the ratio v_{oc}^2/v_{kc}^2 to obtain the curve desired for the determination of F.

This inconvenience becomes on further analysis a remarkable simplification of the work of Schottky. The following development due to the authors is here presented for the first time.

Simplification of the Tuned-Circuit Problem

The power factor of the circuit varies with the thermionic current, but it may be maintained constant by the addition of suitable resistances. Let this be done.

If now we take the expression given by Hull and Williams for the mean square output voltage due to the k-component of the thermionic current, we have

$$\overline{E_k^2} = \tfrac{1}{2}L^2\omega_0^2 A_0^2 C_k^2 \frac{x^2 f(x)}{(1-x^2)^2+r^2x^2}$$

$$= \tfrac{1}{2}L^2\omega_0^2 A_0^2 C_k^2 \frac{x^2}{(1-x^2)^2+r^2x^2} \times \frac{v_{0c}^2}{v_{kc}^2}\phi(x)$$

where $r = R/L\omega_0$. But

$$\frac{v_{0c}^2}{v_{kc}^2} = \frac{\omega_k^2 + (L^2/R^2)(\omega_k^2-\omega_0^2)^2}{\omega_k^2}$$

$$= \frac{(1-x^2)^2+r^2x^2}{r^2x^2}.$$

So that

$$\overline{E_k^2} = \frac{L^2A_0^2}{2R^2C^2} C_k^2 \phi(x)$$

Substituting for C_k^2 its value $\overline{C_k^2} = (4\iota_0\epsilon\omega_0/2\pi)dx$ we obtain for the total mean square output voltage

$$\overline{E^2} = \Sigma\overline{E_k^2} = \frac{L^2A_0^2}{2R^2C^2} \times \frac{4\iota_0\epsilon\omega_0}{2\pi} \Sigma\phi(x)dx$$

$$= \frac{2\iota_0\epsilon L^2A_0^2}{R^2C^2} \int_0^\infty \psi(\nu)d\nu$$

where ν (the frequency) $= \omega/2\pi$; $\psi(\nu) = \phi(x)$; and $dx = d(\omega/\omega_0) = (1/\omega_0)\, d(2\pi\nu) = (2\pi/\omega_0)d\nu$. $\int\psi(\nu)d\nu$ becomes simply the area under the curve $\phi(x)$ plotted against frequency. If we call this area A, the above equation yields

$$\overline{E^2} = 2\iota_0\epsilon L^2A_0^2A/R^2C^2$$

If as before we introduce a voltage v_1 which causes the same output as the shot-effect, we have $i = v_1/R$ where i is the current in the tuned circuit and v_1 has the frequency $\nu_0 = \omega_0/2\pi$, and the condenser voltage v_c is $i/\omega_0 C$ or $v_1/RC\omega_0$. Also $\overline{E^2} = A_0^2v_c^2 = A_0^2v_1^2/R^2C^2\omega_0^2 = 2\iota_0\epsilon L^2A_0^2A/R^2C^2$ so that $\epsilon = v_1^2/2L^2\omega_0^2\iota_0A$.

It may be noted that by this means we may avoid the complicated evaluations of the original shot-integral. Also, since v_1 is introduced by a current I_1 flowing through an inductance L_1 of negligible resistance, we have

$$\epsilon = L_1^2I_1^2\omega_0^2/2L^2\iota_0A\omega_0^2 = L_1^2I_1^2/2L^2\iota_0A$$

This measurement is independent of all frequency measurements except those of frequency differences for the area A. This results in the possibility of much greater accuracy than does the method of substitution.

Analysis of the General Case

Hitherto all the work that has been published on shot-effect has considered tuned circuits only, and indeed the preceding development is of the same class. The following shows however that a general solution may be made which is applicable to all circuits suitable for the production of shot-effect. This may be stated in general as an inductive resistance in parallel with a capacitance. A series capacity obviously makes impossible the application of an accelerating potential to the anode.

The above discussions apply to circuits tuned to the resonance frequency, ν_0, of the amplifier, and of such small resistance that R^2 may be neglected in comparison to $L^2\omega_0^2$. The following discussion is more rigorous and completely general for the circuit in that it involves no assumption regarding the relative magnitude of R, L, and C, and makes no mention of a natural period of the circuit. It applies, indeed, equally well to circuits which are aperiodic. In the following, ω_0 will refer to 2π times the resonance frequency of the amplifier, and has no connection with the natural period (if one exists) of the circuit where the shot-effect is generated. It is here assumed that the power factor of the circuit is invariant, and this condition, as has been pointed out above, may be realized.

We have as above, $\iota_k = C_k \sin(\omega_k t + \phi_k)$ whence $\overline{\iota_k^2} = \frac{1}{2}C_k^2$. If the shot-current be caused to flow through an impedance Z, the mean square voltage produced across it by the k-component is given by

$$\overline{v_k^2} = \tfrac{1}{2}Z_k^2 C_k^2$$

and

$$\overline{E_k^2} = \tfrac{1}{2}Z_k^2 C_k^2 A_0^2 f(x)$$

where A_0 and $f(x)$ have the significance assigned above.

Thus

$$\overline{E^2} = \tfrac{1}{2}A_0^2 \Sigma Z_k^2 C_k^2 f(x).$$

If the impedance is of the form shown in Fig. 1, and $\phi(x)$ is the curve obtained as power output when the input current I_1 through the inductance L_1 is maintained constant, we have, where i is the current generated in the circuit, $i = L_1 I_1 \omega/\xi$ where ξ is the series impedance of the circuit, $\xi = \sqrt{R^2+(L\omega - 1/\omega C)^2}$. So that $i = L_1 I_1 \omega/\sqrt{R^2+(L\omega-1/\omega C)^2}$ and $v_c = L_1 I_1 \omega/\omega C\sqrt{R^2+(L\omega-1/\omega C)^2}$ where v_c is the condenser voltage. Thus

$$\frac{v_{0c}^2}{v_{kc}^2} = \frac{L_1^2 I_1^2}{C^2\left[R^2+(L\omega_0 - 1/\omega_0 C)^2\right]} \times \frac{C^2\left[R^2+(L\omega_k - 1/\omega_k C)^2\right]}{L_1^2 I_1^2}$$

where $\nu_0=\omega_0/2\pi$, is the resonance frequency of the amplifier and v_{oc} the condenser voltage at ν_0.

If, as above, we set $x=\omega_k/\omega_0$,

$$\frac{v_{0c}^2}{v_{kc}^2}=\frac{1}{R^2C^2\omega_0^2+(1-LC\omega_0^2)^2}\times\frac{R^2C^2\omega_0^2x^2+(1-LC\omega_0^2x^2)^2}{x^2}$$

Now from our method of its derivation

$$\phi(x)=\frac{E_k^2}{E_0^2}=\frac{v_{kc}^2A_0^2f(x)}{v_{0c}^2A_0^2}$$

So that $f(x)=\phi(x)v_{oc}^2/v_{kc}^2$; $\overline{E^2}=\frac{1}{2}A_0^2\Sigma Z_k^2C_k^2f(x)$ where $Z_k^2=(R^2+L^2\omega_k^2)/[R^2C^2\omega_k^2+(1-LC\omega_k^2)^2]$ and $\overline{C_k^2}=4\iota_0\epsilon\omega_0dx/2\pi$.

So that

$$\overline{E^2}=\tfrac{1}{2}A_0^2\,4\iota_0\epsilon(\omega_0/2\pi)\int_0^\infty\frac{R^2+L^2\omega_k^2}{R^2C^2\omega_k^2+(1-LC\omega_k^2)^2}f(x)dx.$$

$$=2A_0^2\iota_0\epsilon(\omega_0/2\pi)\int_0^\infty\frac{R^2+L^2\omega_0^2x^2}{R^2C^2\omega_0^2x^2+(1-LC\omega_0^2x^2)^2}\times\frac{v_{0c}^2}{v_{kc}^2}\phi(x)dx$$

$$=\frac{2A_0^2\iota_0\epsilon}{R^2C^2\omega_0^2+(1-LC\omega_0^2)^2}\times\frac{\omega_0}{2\pi}\int_0^\infty\frac{R^2+L^2\omega_0^2x^2}{x^2}\phi(x)dx\cdots$$

$$=\frac{2A_0^2\iota_0\epsilon}{R^2C^2\omega_0^2+(1-LC\omega_0^2)^2}\times\frac{\omega_0}{2\pi}\left[\int_{1-\kappa}^{1+\kappa}\frac{R^2}{x^2}\phi(x)dx+\int_{1-\kappa}^{1+\kappa}L^2\omega_0^2\phi(x)dx\right]$$

where $1-\kappa$ to $1+\kappa$, $\kappa\ll1$, are the limits over which the integration need be extended to include all values of x for which $\phi(x)\neq0$. In

$$\int_{1-\kappa}^{1+\kappa}\phi(x)dx/x^2$$

set $z=1/x$, $dz=-dx/x^2$. Then if $\phi(x)$ is symmetric with respect to $x=1$, so that $\phi(1/(1+\delta))=\phi(1-\delta)=\phi(1+\delta)$,

$$\int_{1-\kappa}^{1+\kappa}\phi(x)dx/x^2=\int_{1-\kappa}^{1+\kappa}\phi(1/z)dz=\int_{1-\kappa}^{1+\kappa}\phi(z)dz=\int_{1-\kappa}^{1+\kappa}\phi(x)dx$$

since a definite integral is independent of the variable of integration.

$$\overline{E^2}=\frac{2A_0^2\iota_0\epsilon}{R^2C^2\omega_0^2+(1-LC\omega_0^2)^2}\times\frac{\omega_0}{2\pi}\left[\int_{1-\kappa}^{1+\kappa}R^2\phi(x)dx+\int_{1-\kappa}^{1+\kappa}L^2\omega_0^2\phi(x)dx\right]$$

$$=\frac{2A_0^2\iota_0\epsilon(R^2+L^2\omega_0^2)}{R^2C^2\omega_0^2+(1-LC\omega_0^2)^2}\left[\frac{\omega_0}{2\pi}\int_{1-\kappa}^{1+\kappa}\phi(x)dx\right]$$

$$=\frac{2A_0^2\iota_0\epsilon(R^2+L^2\omega_0^2)A}{R^2C^2\omega_0^2+(1-LC\omega_0^2)^2}$$

$$=2A_0^2Z_0^2\iota_0\epsilon A$$

where Z_0 is the impedance of the shot-circuit at the resonance frequency of the amplifier, and A has the same significance as formerly. This discussion is independent of the relative magnitudes of L, R and C.

If ξ be the series impedance of the circuit at the frequency ν_0, we have, where a voltage v_1 is introduced into the circuit by the current I_1 flowing through the inductive reactance $L_1\omega_0$, $i=v_1/\xi=L_1I_1\omega_0/\xi$ where i is the current in the circuit. The condenser voltage

$$v_c=i/\omega_0C=L_1I_1\omega_0/\omega_0C\xi=L_1I_1/\xi C$$

If the voltage v_1 introduced into the circuit causes the same mean square output voltage $\overline{E^2}$, as is occasioned by the shot-effect,

$$A_0^2v_c^2=\overline{E^2}=2Z_0^2A_0^2\iota_0\epsilon A$$

or substituting for v_c its value given above,

$$A_0^2L_1^2I_1^2/\xi^2C^2=2A_0^2Z_0^2\iota_0\epsilon A$$

Whence $\epsilon=L_1^2I_1^2/2Z_0^2\xi^2C_0^2A$. For this type of system $\xi^2=R^2+(L\omega_0-1/\omega_0C)^2$.

If this be applied to a periodic circuit of small resistance having a natural period $2\pi/\omega_0$, we have $Z_0=L/RC$, $\xi=R$, so that $\epsilon=L_1^2I_1^2/2(L^2/R^2C^2)R^2C^2\iota_0A=L_1^2I_1^2/2L^2\iota_0A$ which is precisely the result obtained for this type of circuit in the previous discussion.

Analysis for a Pure Resistance

The experimental part of this investigation deals with the case in which the shot-circuit is a non-inductive resistance R. Since a substitution method was used in these measurements, a modification of the general method of the preceding paragraph becomes necessary. No effects of energy fed back from the output into this resistance were to be observed, so a method of substitution should lead to correct experimental results. The method of computation follows closely those previously outlined.

If, as above, the thermionic current traverses the resistance R, we have for the k-component of the Fourier series into which the whole current may be developed

$$\iota_k=C_k\sin(\omega_kt+\phi_k)$$

and $v_k=R\iota_k$ where v_k is the voltage introduced across the resistance by ι_k. Thus $v_k=RC_k\sin(\omega_kt+\phi_k)$ and $\overline{v_k^2}=\frac{1}{2}R^2C_k^2$. If $\overline{E_k^2}=v_k^2\,A_0^2f(x)$ where $\overline{E_k^2}$, A_0 and $f(x)$ have the significance previously assigned, then the total mean square voltage output

$$\overline{E^2}=\overline{\Sigma E_k^2}=A_0^2\Sigma\overline{v_k^2}f(x)$$
$$=\tfrac{1}{2}R^2A_0^2\Sigma C_k^2f(x)$$

If, as before, we substitute for C_k^2 its value

$$\overline{C_k^2} = 4\iota_0\epsilon\omega_0 dx/2\pi$$

we have

$$\overline{E^2} = \tfrac{1}{2}R^2A_0^2 4\iota_0\epsilon(\omega_0/2\pi)\int_0^\infty f(x)dx$$

where A is the area under the curve which represents relative voltage-square amplification plotted against frequency.

If now the system producing the shot-effect be disconnected and a voltage v_1 at the resonance frequency, ν_0, of the amplifier be applied to the input, it becomes after amplification A_0v_1. v_1 may be adjusted so that the output has the same r.m.s. value as that occasioned by the shot-effect.

We have then $\overline{E^2} = A_0^2v_1^2 = 2R^2A_0^2\iota_0\epsilon A$ whence $\epsilon = v_1^2/2R^2\iota_0 A$.

The Resistance R

The selection of a resistance suitable for the measurement of these effects is a matter of some interest. High resistances of vanishingly small self-inductance are readily obtainable. These usually consist of a paper base with a coating of India ink, Aquadag or other similar substance, but unfortunately they exhibit the well-known property of fuzziness. That is, when carrying a direct current from a battery the resistance is not constant, but exhibits a random fluctuation.

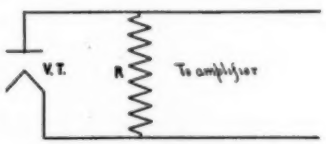

Fig. 2. Diagram of aperiodic circuit used in obtaining measurements submitted.

The resistance used in this work was a line of graphite on the etched surface of a glass tube ½ inch in diameter and 3 inches long. Investigation showed that this when properly prepared had a constant resistance, and was in every way suitable.

Capacity and Leakage Effects

One could not assume, however, that the magnitude of R was the impedance in the path of the thermionic current. If we examine the circuit, we note that we have in parallel with R the leakage across the socket and tube V.T. and across the amplifier input as well as attendant capacity effects. Thus it seemed necessary to measure the impedance

of the circuit as it was actually used. The capacity effects alone are dependent on the frequency, and if these are small and the resonance curve not too broad, it will make little difference at what point in the region the impedance is measured. If it be measured at the lowest frequency of the resonance curve, it will be too great, at the highest, too small. Hence it was measured at such a frequency that an ordinate through this point passes through the center of area of the region under the resonance curve. If we consider that the impedance of the circuit is the one obtained in this way, and that it is constant throughout the pass-band of the amplifier, the error introduced is vanishingly small.

Thus in the expression for $\overline{E^2}$ we shall write Z,—where Z is the impedance obtained under the conditions mentioned above,—in place of R in our former consideration. The value of $\overline{E^2}$ then becomes

$$\overline{E^2} = 2Z^2 A_0^2 \iota_0 \epsilon A$$

or solving for ϵ as before,

$$\epsilon = v_1^2 / 2Z^2 \iota_0 A$$

Measurement of v_1

The measurement of v_1 was carried out by precisely the method used by Hull and Williams,[6] and it will be discussed here very briefly. The method utilizes the inductive drop in a short length of a long straight brass rod surrounded by a concentric cylindrical return conductor. Hull and Williams have shown that if the cylindrical return be connected to the central rod by a block of brass or other material of small resistance, carefully sweated in so that it makes contact with the cylinder at its inner edge, then the field is uniform right up to the inner surface of the disc, and hence this may be considered the zero point and all measurements made therefrom. The inductance per centimeter of such an arrangement is

$$L_{cm} = 2\log_e(R/r) \text{ e.m.u.}$$

where R is the radius of the cylindrical return and r the radius of the central rod.

In the apparatus used $R/r = 6$, so that $L_{cm} = 2 \log_e 6 \times 10^{-9}$ henries, and the inductance per length used, $-l$, which has been referred to formerly as L^1, $L_1 = 2\, l \log_e 6 \times 10^{-9}$ henries. Thus if a current I_1 from a generator traverses this inductance, v_1, the potential across it will be $v_1 = L_1 I_1 \omega$ and in particular when the generator frequency is the same as the resonance frequency of the amplifier,

$$v_1 = L_1 I_1 \omega_0 = 2\, l \log_e 6 \times 10^{-9} I_1 \omega_0$$

The design of the apparatus permits the use of 3, 6, 9, 12, 15, 18, 21, or 24 centimeters of length since it is tapped at these points.

The Amplifier

The amplifier is a five stage cascade tuned-impedance-coupled system. The impedances consist of 400 turn coils wound on hard rubber cores 1 inch in diameter and $\frac{1}{2}$ inch in length, the coils being in parallel with suitable capacities. The tubes used in the amplifier are screen grid tubes similar to those used by Hull and Williams, and supplied through the courtesy of Dr. Hull of the Research Laboratories of the General Electric Company. Each stage is contained in a metal case which shields from outside influence, and all high voltage lines are carefully filtered. The amplification used was not measured but was estimated from previous experience to be a voltage amplification of about 10^6.

Detection

The method of detection is perhaps deserving of special mention since it is not precisely that used by Hull and Williams in obtaining the results they have published, but a method later devised by them and used in some more recent work.

A coil, whose ends are connected across the heater element of a 900 ohm vacuum thermocouple, is placed in the field of the coil in the plate circuit of the last amplifier tube. The output is read on a galvanometer connected to the couple side of the thermocouple. These leads are connected inside the case of the amplifier by a large condenser. Investigation showed that the apparatus obeys the square detection law within the limit of error of the measurements; that is, the galvanometer reading is proportional to the power input.

Experimental Procedure

The method of finding the particular v_1 which corresponds to a certain ι_0 in our formula, is as follows:

The thermionic current ι_0 is caused to traverse the impendance Z. The voltage across Z is applied to the input of the amplifier and the deflection of the galvanometer in the output noted. This system is now disconnected and the voltage v_1 across the self-inductance L_1 is used as input. If v_1 be now adjusted so that the output galvanometer experiences the same deflection as before, we have, where v_1 has the frequency ν_0

$$A_0^2 v_1^2 = \overline{E^2} = 2Z^2 A_0^2 \iota_0 \epsilon A$$

or $\epsilon = v_1^2/2Z^2\iota_0 A$. We have shown before that $v_1 = 2\,\mathrm{l}\,\log_e 6\times 10^{-9}\, I_1\omega_0$. The determination of l consists in the selection of a suitable tap on L_1 so

that to produce the desired voltage, the current I_1 should be of a magnitude convenient for measurement.

The Generator System

The current is generated in a movable coil placed in inductive relationship to another coil carrying the generator output. Capacity coupling is avoided by the use of a static screen. The mutual inductance and hence I_1 is altered by rotating the coil. The measurement of the current is effected by the use of a vacuum thermocouple together with a calibration curve.

A large cage of wire mesh about the amplifier and a smaller one about the generator prevent interaction. The source of energy for each system is within the cage that contains it.

Experimental Work

The first work with this aperiodic circuit was carried out at a frequency of about 50 kilocycles. The effect was easily perceptible, but certain other considerations led to the use of higher frequencies. When the amplifier was actuated by the shot-voltage, the output galvanometer exhibited random fluctuations in deflections. These were believed to be other than variations in battery voltage, since this random effect disappeared when the generator system was used as input. The magnitude of these fluctuations was decreased by the introduction of a thermocouple of larger thermal capacity, but they still caused such inconvenience that, while the mean of a set of readings yielded results of the proper order of magnitude, individual readings would differ by as much as twenty percent. This phenomenon is perhaps a consequence of the flicker effect discussed by Schottky in his recent paper.[8] A change to higher resonance frequency led to the disappearance of this annoyance. The first work which is to be presented here was carried out at a frequency of 146 kilocycles.

The resistance used had a value of 48300 ohms, and a measurement of the impedance by the method outlined in a preceding paragraph yielded the value 34500 ohms.

The Area A

The area A was to be determined as the area under the curve representing relative voltage square amplification plotted against frequency. Since the apparatus obeys the square detection law, the reading of the output galvanometer at any fixed frequency is proportional to the power

[8] W. Schottky, Phys. Rev. **28**, 74-103 (1926).

input. If a voltage v_1 of constant magnitude and varying frequency be applied to the input, the galvanometer deflections, divided by the deflection for ν_0, will give the ordinates of the required curve.

In actual practice it is the input current I_1, and not v_1 which is maintained constant. If $\phi(\nu)$ be the curve obtained in this way, and $f(\nu)$ the curve required, we have

$$\phi(\nu_k) = A_0^2 v_k^2 f(\nu_k)/A_0^2 v_0^2$$

where v_k is the value of v_1 at the frequency ν_k. Thus

$$f(\nu_k) = (v_0^2/v_k^2)\phi(\nu_k) = (L_1^2 I_1^2 \omega_0^2/L_1^2 I_1^2 \omega_k^2)\phi(\nu_k) = \phi(\nu_k)\omega_0^2/\omega_k^2.$$

That is, each ordinate of the experimentally determined curve $\phi(\nu_k)$ must be multiplied by the ratio ω_0^2/ω_k^2.

This correction produces an increase in the ordinates on one side of the resonance frequency, and a decrease on the other. The change in area is quite insignificant, but was taken into account in obtaining the value of A.

TABLE I

Summary of measurements leading to the determination of electron charge. v_1 is given in microvolts ϵ in coulombs $\times 10^{19}$

t_0	I_1	l	v_1	Z	A	ϵ
		Frequency = 146 kilocycles				
.206	1.070	9	31.7	34500	12880	1.587
.310	1.320	9	39.1	34500	12880	1.605
.367	1.432	9	42.4	34500	12880	1.595
.404	1.500	9	44.4	34500	12880	1.590
.447	1.587	9	46.7	34500	12880	1.590
.508	1.260	12	49.7	34500	12880	1.586
.614	1.387	12	54.7	34500	12880	1.590
.715	1.497	12	59.1	34500	12880	1.591
.811	1.274	15	62.8	34500	12880	1.587
					Ave	1.5912
		Frequency = 114.25 kilocycles				
.206	1.019	9	23.6	36870	6231	1.595
.310	1.248	9	28.9	36870	6231	1.590
.404	1.425	9	33.0	36870	6231	1.590
.417	1.500	9	34.7	36870	6231	1.593
.508	1.198	12	37.0	36870	6231	1.589
					Ave	1.5914

EXPERIMENTAL DIFFICULTIES AND LIMIT OF ERROR

A consideration of the foregoing results leads to a matter of some interest, viz. how far experimental difficulties may be overcome and the resulting limit of error that may be placed on results obtained by this method.

Variation in battery voltage is a source of some annoyance, since small variations, with an amplification of the order of magnitude used, produce very appreciable changes in results. If sufficient care be taken to avoid this difficulty, individual readings vary between narrow limits. It seems that if calibrations could be made and maintained with such accuracy that the systematic error were known to be negligible, then considerable precision might be anticipated.

The region of uncertainty in the preceding measurements is about 1 percent.

It will be noted that the mean values obtained agree, within the limit of experimental error, with the value given by Millikan,—1.5913×10^{-19} coulombs.

Space Charge

A study of the effect produced by the probability fluctuations of thermionic emission in a vacuum tube may be carried out under conditions other than those of temperature limitation. The foregoing work is of interest in that it leads to a determination of the electronic charge ϵ; investigation under other conditions may lead to some knowledge of the effect produced by amplifier tubes in actual use.

The tube used in the preceding work was a Radiotron U.X. 120. The grid and plate together formed the anode and were maintained at a voltage which exceeded that of the cathode by some hundred to a hundred and twenty volts. This straight filament tube was employed to eliminate suspicion of residual space charge. Fear was experienced that, with a filament of the Λ type such as is used in the Radiotron U.V. 201A, even with as high anode potentials as one might apply, some space charge might still exist in the region where the two branches of the filament lie near together. The following investigation will show that space charge may be eliminated even with a filament of the M type, such as is used in the U.X. 112 tube.

In customary use the potential of the grid is maintained at a much lower value than in the preceding work and the magnitude of the probability fluctuations varies proportionately.

For the following curves, the anode potential and the space current were maintained constant, the filament current and grid potential being the variables.

These curves which, within the limits of experimental error are straight lines, show that if account be taken of the change in tube impedance, very little variation occurs in the distribution of electrons striking the anode when the space charge, but not the plate current, is

increased. It would seem that the diminution of shot-voltage experienced by others has been due in a great measure to higher current densities in the tube rather than to an accumulation of electrons in the region of the filament.

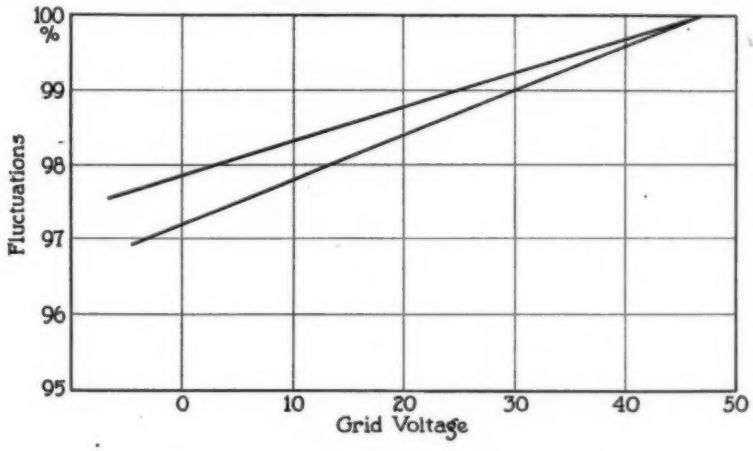

Fig. 3. Curves showing decrease of probability fluctuations with an increase of space charge. Ordinates represent percent fluctuations compared with those produced under conditions of temperature limitation,—the abscissae show corresponding grid voltages in volts. Due account is taken of the change in tube impedance. Upper curve taken for plate current of 1 m.a., lower, 2 m.a.

Discussion of Results

The theoretical work of this paper has a significance of fundamental importance in connection with the accuracy one may attain in these measurements. The analysis for the tuned circuit makes the measurements independent of a determination of the resonance frequency, and the results of this are very far-reaching. A wave-meter measuring ranges of frequencies is always subject to possible changes in the position of the mechanism, and resulting changes in calibration. Any variation which is likely to occur will affect the actual frequency reading far more than a reading of frequency differences. The method permits the use of a totally uncalibrated crystal oscillator. The crystal will maintain a definite frequency, and even if this be unknown, frequency differences may be read by a method of beat notes and sound standards. These latter may be known and maintained with great accuracy.

The analysis eliminates all necessity of a knowledge of the resistance of the circuit. Even an exact measure, in ohms, of resistance differences is unnecessary. If an impulse be applied to the circuit, and the condenser voltage to a detector tube, and if further conditions be adjusted so that

the cessation of the thermionic current, and the simultaneous introduction of a resistance produces no change in the detector action, then the necessary condition is fulfilled.

The labor of computation is greatly reduced, since that required to obtain the area A is negligible compared with the manipulation entailed in the evaluation of F.

The use of an aperiodic circuit possesses some advantages. It is remarkably less subject to regeneration effects than is a tuned circuit. The accuracy of results with a periodic system depends in a large measure on a precise tuning of the circuit. This is entirely eliminated, increasing both ease of manipulation and freedom from error. Especially at low frequencies, where capacity effects become negligible, may a higher plate impedance be attained with a resistance than is possible for a tuned circuit.

Regarding the values given for electronic charge, the first set, while taken with considerable care, does not represent so great precision as the second. The authors hope to be able to publish in the near future a series of results whose region of uncertainty will be even more narrowly limited.

UNIVERSITY OF MICHIGAN,
August 14, 1926.

AN EFFECT OF LIGHT ON THE ELECTRON EMISSION FROM HOT FILAMENTS*

By W. H. Crew

Abstract

Photo-electric currents from hot, oxide-coated platinum filaments.—The increase in the electron emission from hot, oxide-coated platinum filaments when illuminated by the full radiation from a water-cooled quartz mercury arc was measured, for different filament temperatures, as a function of potential between filament and anode. The photo-electron currents were large enough to be readily measurable with a galvanometer. Measurements on one filament showed the photo-electron current increasing with potential to a maximum at about 14 volts. For another filament, twice as thick, the maxima were between 2 and 4 volts. In the case of both filaments increasing the temperature shifted the maximum to lower values of potential. No *photo-electric fatigue* was observed. By the use of various absorbing screens and different sources of light it was found that the photo-currents are, for the most part, due to radiations of wave-lengths shorter than λ3000; but that the *long wave-length limit* is somewhat above that value.

Photo-electron currents from other filaments.—In all, four types of filaments were tried: (a) oxide-coated platinum; (b) plain platinum; (c) oxide-coated tungsten; (d) plain tungsten. Of these, only the oxide-coated filaments gave an appreciable emission due to the light.

The possible source of the photo-electrons is discussed and calculations are made as regards their velocity distribution. Results suggest that the action of the light is to free electrons from a thin film of metal of which the work-function varies with temperature of the filament.

THE photo-electric effect, discovered by Hertz in 1887, was first observed in the case of metals by Hallwachs in the following year. This phenomenon has since been studied with regard to its variation with temperature by Stoletow,[1] Zeleny,[2] Thomson,[3] Millikan,[4] Piersol,[5] and others. In 1921, Merritt[6] extended some experiments previously described by Case,[7] and found that in one instance the heating to incandescence of an oxide-coated filament increased its photo-electric emissivity 1400-fold. Obviously, then, photo-currents obtained from hot oxide-coated filaments are enormous when compared with those obtained at normal temperatures, and may be studied by use of a moderately sensitive galvanometer.

* Published by permission of the Director of the Naval Research Laboratory.

[1] A. Stoletow, Comptes rendus **108**, 1241 (1889).
[2] J. Zeleny, Phys. Rev. **12**, 321 (1901).
[3] J. J. Thomson, Cond. of Elec. Through Gases, p. 239.
[4] R. A. Millikan, Phil. Mag. **14**, 188 (1907).
[5] R. J. Piersol, Phys. Rev. **8**, 238 (1916).
[6] E. Merritt, Phys. Rev. **17**, 525 (1921).
[7] T. W. Case, Phys. Rev. **17**, 398 (1921).

In view of recent work done by Rouse and Giddings[8] and also by Foote and Mohler,[9] the possibility was entertained that the phenomenon might be a result of a secondary effect of the light. More precisely, Rouse and Giddings found that the radiation λ2536 alone produced positive ions in mercury vapor; and Foote and Mohler showed that positive ions could be made to increase greatly the emission from a filament by neutralizing the limiting space charge thereof. Accordingly, experiments were made to see whether the increase of photo-emission with increase of temperature was due directly to the action of the light on the filament or indirectly to the production of positive ions in the surrounding vapor.

A description of the experimental examination of this point, in which the direct action of the light was found to prevail, and a further study of the photo-emission from hot filaments embrace the chief endeavors of this paper.

Apparatus

A two-electrode vacuum tube, 2.5 cms in diameter, was constructed of Pyrex glass as indicated in Fig. 1. One end of the tube was closed by a quartz window Q, fused on by means of a quartz-Pyrex union. Various

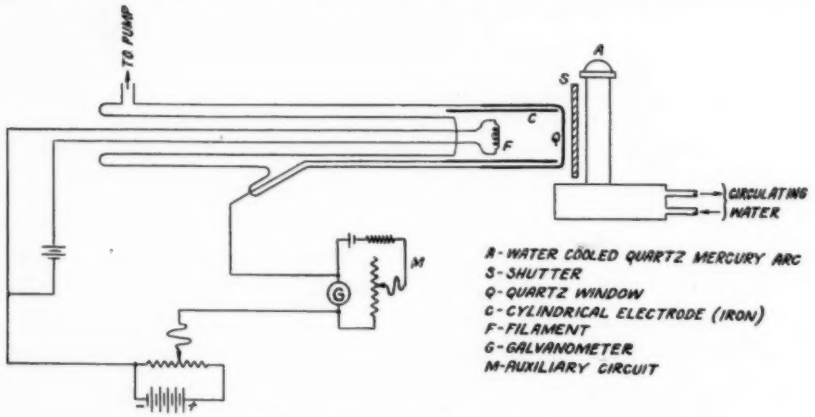

Fig. 1. Diagram of apparatus.

filaments F were used in these experiments and were secured to tungsten leads by means of small clamps made of molybdenum. The plate electrode C was an iron cylinder surrounding the filament. All leads entered the tube through tungsten to glass seals, and no ground glass or wax joints were used.

The evacuating system consisted of a mercury vapor pump backed by a "High-Vac" oil pump, a McLeod gauge, and a liquid-air trap located

[8] C. F. Rouse and G. W. Giddings, Phys. Rev. **25,** 893 (1925).
[9] P. D. Foote and F. L. Mohler, Phys. Rev. **26,** 195 (1925).

next to the tube. For all experiments a pressure of 10^{-6} mm of mercury (per gauge) or better was used.

Various potentials between filament and plate were applied by means of a battery of storage cells and controlled by a potentiometer of the slide wire type. Electronic currents were measured by a Leeds and Northrup high sensitivity low resistance galvanometer, which was capable of measuring the photo-currents from a hot filament, but was practically insensible to the relatively insignificant photo-electric currents from the filament at room temperature. An auxiliary circuit M (Fig. 1) was arranged so that balancing currents could be applied to the galvanometer in order to bring the reading to zero at will. The source of radiation for these experiments was a Cooper-Hewitt quartz mercury arc A cooled by running water. A shutter S was located between the arc and tube to admit the light to the tube as desired.

An electric oven was built to slip over the tube *in situ*. This served not only to bake out the tube but also, in conjunction with the liquid air trap, as a means of removing residual mercury vapor from that part of the apparatus.

Experimental Procedure

In the first set of experiments a strip of platinum foil about 2 mm wide and 10 mm long was used as a filament, and was coated with the oxides of barium and thorium. The tube was then evacuated to a pressure of less than 10^{-6} mm of Hg; and with the pumps running, was thoroughly baked-out for several hours at a temperature of 400°C. After the tube had been allowed to cool, a potential was established such that the electron current was from filament F to plate C, and the galvanometer deflection due to the thermionic current was counter-balanced by the auxiliary circuit M so that the scale reading was zero. The shutter S was then opened, and the total radiation from the mercury arc shone on the filament and caused a deflection of the galvanometer which was noted. A series of readings taken in this manner at different values of applied potential comprised a run, three of which are plotted in Fig. 2. Curve I is a run made before the baking-out process had eliminated the mercury vapor from within the tube. This curve shows a gradual increase of the photo-electron current from zero at 2 volts potential to a saturation value of 4.5 cms deflection at about 6 volts. Curve II is a run made after the mercury vapor had been partly eliminated from the tube, and Curve III is a run made after prolonged baking out had rather thoroughly removed the mercury from the tube. Curves II and III rise almost linearly to a value of photo-electron current at 8 volts potential which is nearly five times as great as that in Curve I.

These curves are taken to show that the removal of mercury vapor from within the tube greatly enhanced the photo-electron emission from the filament, and that therefore this emission was due to the direct action of the light upon the filament and not to a secondary process of ionization of the mercury vapor.

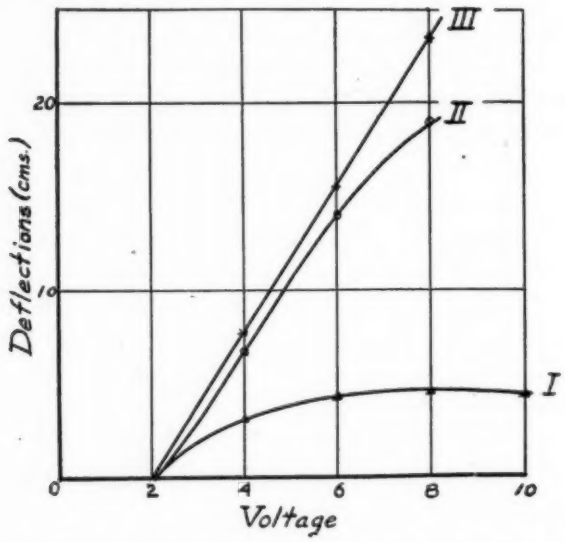

Fig. 2. Photo-electric current from an oxide-coated platinum filament as a function of applied potential.

Operating the tube in the condition in which the mercury vapor had been removed according to the manner previously described, a set of curves, Fig. 3, was obtained giving the photo-current as a function of applied potential for several values of the filament heating current. The curves for which the filament heating current was 2.0 and 2.1 amps. show saturation at about 16 volts; whereas the 2.2 and 2.3 ampere curves rise more abruptly to a maximum value of current and then decrease beyond 14 volts. The 2.4 ampere curve has a maximum ordinate at about 13 volts.

As a check to the consistent performance of the apparatus a run was made at a constant value of 14-volts applied potential at values of filament heating current from 2.0 to 2.4 amps. The galvanometer deflections thus obtained differed from those on the 14-volt ordinate of Fig. 3 by not more than 2 percent. This is taken as an indication of the accuracy with which observations could be repeated.

Upon repeating this experiment with a new oxide-coated platinum filament which was double the thickness of the previous one, the curves of Fig. 4 were obtained. In this case the maxima are seen to be somewhat accentuated and appear in the neighborhood of 3 volts.

There is observed in these curves a shift in the position of the maximum to lower values of applied potential with increase in filament heating current. A similar shift is suggested by the curves of Fig. 3, although the indistinctness of the maxima leaves this fact less certain. However, the shift seems to be perfectly real and consistent.

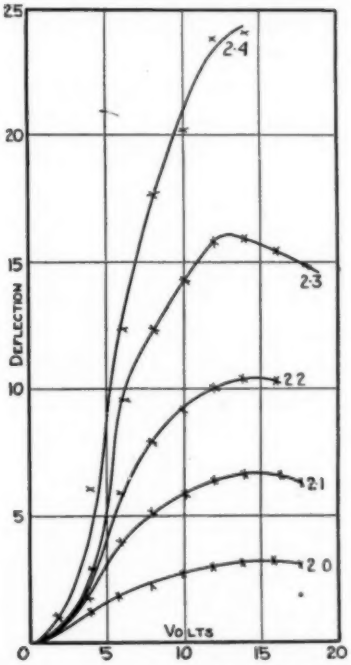

Fig. 3. Photo-electric current from an oxide-coated platinum filament as a function of applied potential for different filament temperatures.

In all of the foregoing curves the points were plotted in order of increasing voltages, and then a few check points were made in the reverse order. The fact that these check points were found to coincide with the curve indicated that the falling off of photo-current at higher potentials was not the result of photo-electric fatigue.

Variation with Wave-length of Incident Light

An attempt was made to observe the photo-emission when the filament was exposed to monochromatic light from a quartz monochromatic illuminator. Because of the reduced intensity of the light and relatively low sensitivity of a galvanometer, no deflections were obtained in this manner. The following experiments indicate, however, that the radiations of shorter wave-lengths are the more effective in producing the photo-emission from the hot filament.

Glass screens of various thickness were interposed between the mercury arc and the quartz window of the tube and the resulting decrease in

galvanometer deflection was noted. A lantern-slide cover glass, 2 mm thick, reduced the deflection due to the transmitted light to zero. Several specimens of thin-blown Pyrex glass admitted of small deflections. These results indicate that the emission of photo-electrons is due primarily to radiations of wave-lengths less than λ3000. A high pressure mercury arc was constructed of Pyrex capillary tubing, and was found to give exceedingly intense radiations down to λ3125. The photo-emission due to this source amounted to about 10 percent of that due to

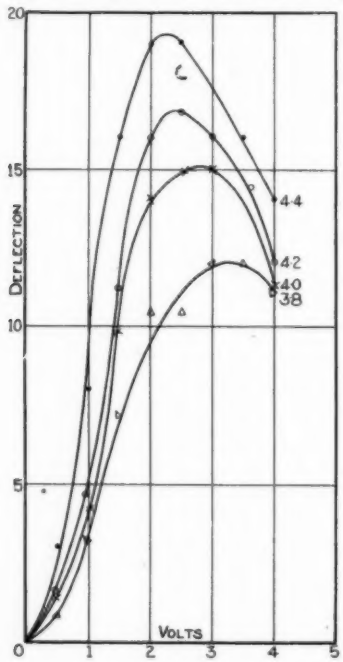

Fig. 4. Photo-electric current from an oxide-coated platinum filament which was double the thickness of that used in obtaining the results shown in Fig. 3.

the quartz arc. These observations indicate that the most effective radiations of the mercury arc are those of shortest wave-length, but that the long wave-length limit (if indeed there is any limit at all) lies above λ3000.

The effect of the removal of mercury vapor from the tube has already been shown (Fig. 2) to increase enormously the emission of photo-electrons. As is well known, mercury vapor in the unexcited condition is capable of absorbing the core of the radiation λ2536. It is probably the reinstating of this portion of the line upon removal of the vapor that is responsible for the increased photo-emission. It has been shown by R. W. Wood that the core of the radiation λ2536 from a mercury arc may be greatly fortified by water-cooling the arc. This was done and

found to increase the emission of photo-electrons about 4-fold. These results indicate that the radiation λ2536 is especially effective in producing the photo-emission.

Observations Made with Other Filaments

Experiments were carried out with the oxide-coated platinum filament replaced by those of (a) plain platinum, (b) plain tungsten, (c) oxide-coated tungsten.

Using a plain platinum filament in the tube and employing the same technique as in the foregoing experiments, no increase of current was observed when the light was admitted to the tube. In fact the thermionic currents from this filament, even when heated to whiteness, were so small as to be barely perceptible on the galvanometer which was used.

The next filament installed was a piece of pure tungsten ribbon 2 mm wide and 0.075 mm thick. When heated this provided ample thermionic currents, but gave no evidence of a photo-emission when light was admitted to the tube. This filament was then given a coating of the oxides of thallium and barium. As a result the thermionic currents were considerably increased and an additional current due to the light from the mercury arc was observed, but this latter was less in proportion to the thermionic current than in the case of the oxide coated platinum. Consequently, it was only by balancing off enormous thermionic currents that the photo-currents became perceptible, and in this condition it was not possible to keep the apparatus steady long enough to make a good run.

This observation with tungsten establishes one important fact; namely, that the photo-electrons are not released from the space-charge; for if they were, it would have been possible to observe photo-electrons with the use of the plain tungsten filament, where there evidently existed an ample space-charge.

Distribution of Electrons

A set of readings was taken with the oxide-coated platinum filament in which the thermionic current was not balanced off. At each value of applied potential, readings were obtained with and without the light shining in the tube, as shown plotted in curves I and II, respectively, of Fig. 5. Curve III is proportional to the difference between curves I and II and represents the current due to the light alone. Here again is observed a maximum value of photo-current at about 2 volts which gradually decreases with higher values of applied potentials. If the logarithm of the ordinates of curve II, Fig. 5, are plotted against the abscissae, one obtains Curve I of Fig. 6. The portion of this curve in the region 0 to 2 volts may be considered as linear and is expressed by the equation

$$\log I_i = CV + k,$$

where I_t is the thermionic current and V is the applied potential. It was recently pointed out by Langmuir[10] that if a current of electrons flowing to a negatively charged collector has a Maxwellian distribution of velocities, the logarithm of this current bears a linear relation to the

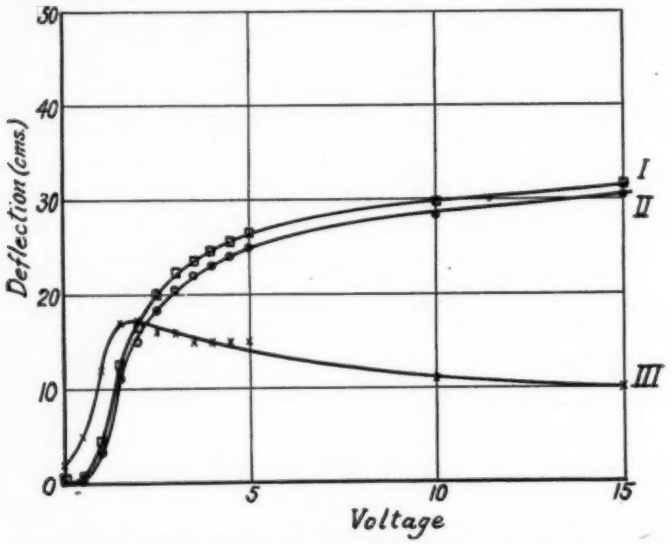

Fig. 5. Curves I and II, total electron emission from an oxide-coated platinum filament with and without light shining in the tube. Curve III is proportional to the difference between I and II.

potential of the collector. This is precisely the condition within the tube below 2 volts applied potential; for at zero volts the cathode is surrounded by a highly negative space-charge. As the plate electrode is made positive up to 2 volts, the negative space-charge is diminished and more electrons flow from filament to grid. This is indicated by the portion of Curve II, Fig. 5, which is concave upwards. Therefore, there is probably a Maxwellian distribution of velocities of the electrons which reach the plate when the thermionic emission is limited by space-charge.

Curve II of Fig. 6 is a semi-logarithmic plot of Curve III of Fig. 5; and here, too, the portion of the curve lying between 0 to 2 volts is linear. From this it may be concluded that the photo-electrons which reach the plate in this region of applied potential have a Maxwellian distribution of velocities.

The slopes of the initial portions of Curves II and I (Fig. 6) are in the ratio 1 to 4. Since the temperature corresponding to the mean velocity of electrons which have a Maxwellian distribution of velocity is inversely proportional to the first power of the slope of the semi-logarithmic plot, the temperature of the photo-electrons in this experiment is of the order 4 times that of the thermo-electrons.

[10] I. Langmuir, Phys. Rev. **26**, 585 (1925).

Discussion of Results

In his Report on Photo-electricity, A. Ll. Hughes[11] gives typical current-voltage curves for the photo-electric emission from pure metals at normal temperatures. In these curves the photo-electric current increases with voltage to a saturation value and there remains constant for higher values of applied potential. The corresponding curves of the present investigation (Figs. 3, 4, 5) are of a distinctly different character, in that the photo-current reaches a maximum and then gradually

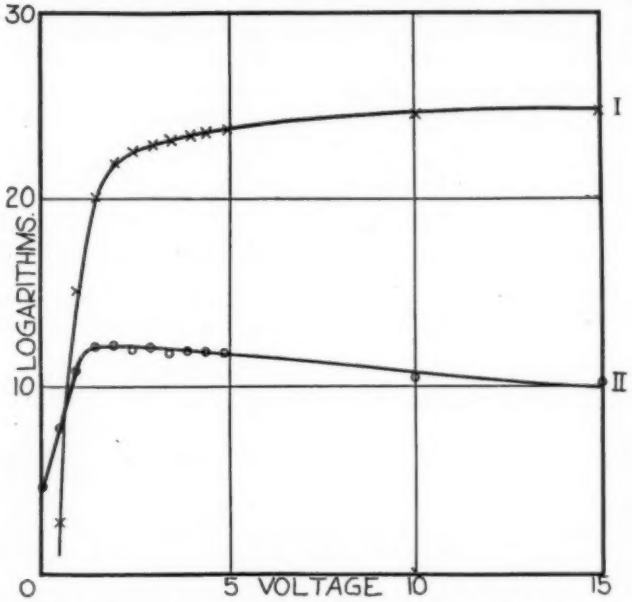

Fig. 6. Semi-logarithmic plot of curves I and II of Fig. 5.

decreases with further increase of applied potential. It remains to be explained, then, how the photo-sensitive surface of a hot oxide-coated filament behaves in order to give rise to a distinct maximum in a current-voltage curve.

A point of view, which has been successfully applied by Ives[12] and by Ives and Johnsrud[13] in the case of pure potassium metal, is to consider a possible change in work-function of the photo-active material. There is evidence of the formation of thin metallic films on the surface of heated oxide-coated filaments. Case[7] has stated that in heating an oxide the pure metal is to some extent set free. J. E. Harris[14] has found that if an oxide-coated platinum filament is glowed in air, some of the platinum

[11] A. Ll. Hughes, Bull. Nat. Res. Council **2**, 10, 92 (1921).
[12] H. E. Ives, J.O.S.A. **8**, 580 (1924).
[13] H. E. Ives and A. L. Johnsrud, J.O.S.A. **11**, 579 (1925).
[14] J. E. Harris, Phys. Rev. **24**, 679 (1924).

enters into chemical combination with the oxides of the coating. If then the filament is glowed in vacuum, the platinum is liberated from the oxide, but remains in the coating in a finely divided state. There is evidence, then, that metal in a pure state may be present in the oxide coating of a filament.

Koller[15] expressed the belief that this metal formed a film over the oxide and was the source of the thermionic emission. The effect of very high temperatures was to partly destroy this film, and consequently decrease the electronic emission; but that subsequent reduction to normal temperatures renewed the metallic film and restored the thermionic emission to its original value.

In the experiments at hand it is quite possible that the photo-electrons come from just such a thin metallic film, and for such a film, it is not difficult to conceive of a value of the work-function much less than for an appreciable thickness of the same metal. It has been definitely found by Koppius[16] that the work-function for oxide-coated platinum decreased with increase of temperature, whereas for plain platinum it was practically constant at 4.80 volts (corresponding to a long wave-length limit $\lambda 2571$).

In direct agreement with this are the observations already described; namely, that large light-induced currents were found only when oxide-coated filaments were used. To account for the maximum observed in the current-voltage curve, it would be necessary to extend this reasoning to the effect that the applied potential in some way changes the work-function of the light-active film. It has been suggested to me by Dr. Millikan that this change may be brought about by the fact that new gases appear because of bombardment and change the work function of the filament.

Although it has been shown that the space-charge alone is not the source of the photo-electrons, it may be that the gradual decrease of the space charge with increase of potential alters the work-function of the metallic film in such a manner as to give rise to the maximum in the current-voltage curve.

This investigation was commenced at the Johns Hopkins University and completed at the Naval Research Laboratory. I am very grateful to Dr. A. Ellett for valuable aid and many generous suggestions. I am indebted to Dr. R. W. Wood, Dr. A. H. Pfund, and Dr. E. O. Hulburt for their interest.

NAVAL RESEARCH LABORATORY,
WASHINGTON, D. C.
September 8, 1926.

[15] L. R. Koller, Phys. Rev. **25**, 671 (1925).
[16] O. Koppius, Phys. Rev. **17**, 395 (1921).

A VELOCITY FILTER FOR ELECTRONS AND IONS

By William R. Smythe*

Abstract

If a charged particle, moving along the x-axis with a velocity v, encounters successively two identical alternating electric fields of frequency ν, which are everywhere perpendicular to the x-axis, it will emerge from the last field undisplaced and traveling in the original direction under the following conditions: (1) Each field has two similar halves whose distance between centers is a; (2) The distance between the fields, center to center, is $D = sa/n$, where s and n are odd integers; (3) The velocity of the particle is $v_0 = 2a\nu/n$. The distribution about the velocity v_0 is computed when particles enter and leave the system through slits of width y_0 on the x-axis. The results show that the emergent beam can be confined to a very narrow velocity range.

Applications of the velocity filter.—Possible applications of the velocity filter, chiefly to positive ray work, are mentioned. It has already proved a successful and convenient substitute for pure magnetic analysis. It can be used to analyze a beam which is inhomogeneous both in mass and velocity when combined with either electric or magnetic deflection methods. The latter combination can be arranged to give a rigorously linear mass scale.

Most methods hitherto used for isolating from a stream of charged particles, moving in a high vacuum, those having a given velocity require the use of a magnetic field. The measurement, maintenance and reproduction of a constant and homogeneous magnetic field is, in many cases, difficult or inconvenient. On the other hand the recent development of radio technique has made it a comparatively simple matter to generate and regulate high frequency oscillating electric fields, so that a method using such fields should prove a valuable addition to those now available for positive ray analysis and similar work.

The first arrangement which suggests itself is an alternating electric field at right angles to the beam. If it were possible to make such a field uniform and sharp edged then those particles whose velocity is such that they pass through the field in a whole number of cycles will evidently have received as much acceleration in one direction as in the other and will emerge parallel to their original direction of motion. Simple considerations show however that they will be displaced from their path by an amount depending on the phase of the field when they entered it. If now a second identical field be placed at such a distance from the first that these particles enter it in opposite phase to that in which they entered the first, then the displacement will be reversed in the second field and the particles will emerge from it undeviated and undisplaced.

* National Research Fellow.

It is impossible in practice to make such a uniform sharp edged field but in the theory which follows it is shown that fields which are neither uniform nor sharp edged and whose actual form is unknown can be used equally well, provided they satisfy certain conditions of symmetry.

I. Theory

CONSIDER a charged particle moving originally along the x-axis with a velocity v which encounters successively two identical alternating fields that are everywhere perpendicular to the x-axis. The origin is chosen at the center of the first field which lies entirely between $-a$ and $+a$. For a given value of x the field strength at any instant is $f(x)\psi(t)$. The wave form of the alternating field may be written

$$\psi(t)=\sum_{r=1}^{r=\infty}C_r\sin(2r\pi\nu t+\phi_r)$$

where ϕ_r is the phase of the rth harmonic as the particle crosses the y-axis and ν is the fundamental frequency. Between $-a$ and $+a$ we may express $f(x)$ as a Fouriers series

$$f(x)=B_0/2+\sum_{q=1}^{q=\infty}B_q\cos(q\pi x/a)+\sum_{p=1}^{p=\infty}A_p\sin(p\pi x/a)$$

The acceleration and y velocity component of the particle of mass m and charge e are respectively

$$\frac{d^2y}{dt^2}=\frac{e}{m}f(x)\psi(t)\text{ and }\frac{dy}{dt}=\frac{e}{m}\int f(x)\psi(t)dt \tag{1}$$

Since the particle has a uniform x velocity component we may write $x=vt$, $dx=vdt$, so that on emerging from the first field

$$\frac{dy}{dt}=\frac{e}{mv}\int_{-a}^{+a}f(x)\psi\left(\frac{x}{v}\right)dx$$

Let $k=2\pi\nu/v$ and substitute values given above for $f(x)$ and $\psi(x/v)$. This gives

$$\frac{dy}{dt}=\frac{e}{mv}\sum_{r=1}^{r=\infty}C_r\int_{-a}^{+a}\left(B_0/2+\sum_{q=1}^{q=\infty}B_q\cos(q\pi x/a)+\sum_{p=1}^{p=\infty}A_p\sin(p\pi x/a)\right)\sin(rkx+\phi_r)dx$$

Integrating this equation gives

$$\frac{dy}{dt}=\frac{e}{mv}\sum_{r=1}^{r=\infty}C_r\left(\left\{\frac{B_0}{rk}+\sum_{q=1}^{q=\infty}(-1)^q B_q\frac{2rka^2}{r^2k^2a^2-q^2\pi^2}\right\}\sin rka\sin\phi_r\right.$$

$$\left.+\sum_{p=1}^{p=\infty}(-1)^p A_p\frac{2p\pi a}{r^2k^2a^2p^2\pi^2}\sin rka\cos\phi_r\right) \tag{2}$$

When $ka=n\pi$, n being an integer, all terms are zero except those for which $rn=q=p$. Let $rn=u$ and the above expression becomes

$$\frac{dy}{dt}=\frac{ae}{mv}\sum_{r=1}^{r=\infty}C_r(B_p u\sin\phi_r+A_p p\cos\phi_r)\frac{2(-1)^p}{\pi}\frac{\sin u\pi}{u^2-p^2}$$

Let $u\to p$ and substitute $ae/mv=n\pi e/kmv=ne/2mv$ and we have

$$\frac{dy}{dt}=\frac{ne}{2mv}\sum_{r=1}^{r=\infty}C_r(B_{rn}\sin\phi_r+A_{rn}\cos\phi_r) \tag{3}$$

The Fouriers coefficients B_{rn} and A_{rn} are

$$B_{rn}=\frac{1}{a}\int_{-a}^{+a}f(x)\cos\frac{rn\pi x}{a}dx \text{ and } A_{rn}=\frac{1}{a}\int_{-a}^{+a}f(x)\sin\frac{rn\pi x}{a}dx.$$

If we make $f(x-a)=f(x)$ and if rn is an odd integer then both B_{rn} and A_{rn} are zero because

$$f(x-a)\cos\frac{rn\pi(x-a)}{a}=-f(x)\cos\frac{rn\pi x}{a}$$

and

$$f(x-a)\sin\frac{rn\pi(x-a)}{a}=-f(x)\sin\frac{rn\pi x}{a}$$

Thus particles emerging from the first field will have no y velocity component if there are only odd harmonics in the alternating field, if $f(x-a)=f(x)$, and if the velocity of the particle is

$$v_0=2av/n \tag{4}$$

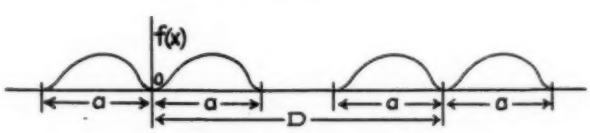

Fig. 1.

where v is the frequency of the alternating field, $2a$ is the length of the field, and n is an odd integer. A form of $f(x)$ which meets the above requirements is shown in Fig. 1.

Displacement in Fields

The y velocity component at a point x in the first field is, from Eq. (1),

$$\frac{dy}{dt}=\frac{e}{mv}\sum_{r=1}^{r=\infty}C_r\int_{-a}^{x}\Big(B_0/2+\sum_{q=1}^{q=\infty}B_q\cos(q\pi x/a)+\sum_{p=1}^{p=\infty}A_p\sin(p\pi x/a)\Big)\sin(rkx+\phi_r)dx$$

The displacement on emerging from the first field will be

$$Y=\frac{1}{v}\int_{-a}^{+a}\frac{dy}{dt}\,dx$$

Integrating this twice we obtain finally

$$Y=\frac{a^2e}{mv^2}\sum_{r=1}^{r=\infty}C_r\left\{\begin{aligned}&\frac{B_0}{r^2k^2a^2}(-\sin rka\cos\phi_r+rka\cos(rka-\phi_r))\\&+\sum_{q=1}^{q=\infty}(-1)^q2B_q\Big[\frac{1}{r^2k^2a^2-q^2\pi^2}\Big(\frac{-(r^2k^2a^2+q^2\pi^2)}{r^2k^2a^2-q^2\pi^2}\sin rka\cos\phi_r\\&\qquad+rka\cos(rka-\phi_r)\Big)\Big]\\&+\sum_{p=1}^{p=\infty}(-1)^p2A_p\Big[\frac{1}{r^2k^2a^2-p^2\pi^2}\Big(\frac{2rka\,p\pi}{r^2k^2a^2-p^2\pi^2}\sin rka\sin\phi_r\\&\qquad+p\pi\sin(rka-\phi_r)\Big)\Big]\end{aligned}\right\}\tag{5}$$

When $ka=n\pi$ all the first terms in the above square brackets drop out except those for which $rn=q=p$. In this case let $rn=u$ and let $u\to p$. Evaluating the indeterminate form gives eventually the following expression in which $p\neq rn$, $q\neq rn$, $ka=n\pi$, and rn is odd.

$$Y=\frac{a^2e}{mv^2}\sum_{r=1}^{r=\infty}C_r\left\{\begin{aligned}&-\Big(\frac{B_0}{r^2n^2\pi^2}+\sum_{q=1}^{q=\infty}(-1)^q\frac{2B_q}{(r^2n^2-q^2)\pi^2}\Big)rn\pi\cos\phi_r\\&\qquad+\sum_{p=1}^{p=\infty}(-1)^p\frac{2A_p}{(r^2n^2-p^2)\pi^2}\,p\pi\sin\phi_r\\&+\frac{B_{rn}}{2rn\pi}(\cos\phi_r+2rn\pi\sin\phi_r)+\frac{A_{rn}}{2rn\pi}(\sin\phi_r+2rn\pi\cos\phi_r)\end{aligned}\right\}$$

But we have chosen rn odd and made $f(x-a)=f(x)$ so that B_{rn} and A_{rn} are zero and odd values of q and p drop out, since for them B_q and A_p are also zero. Substituting the value $a^2e/\pi mv^2=(nv/2\nu)^2\ e/\pi mv^2=n^2e/4\pi mv^2$ gives the equation

$$Y=\frac{n^2e}{4\pi mv^2}\sum_{r=1}^{r=\infty}C_r\left\{-\left(\frac{B_0}{rn}+\sum_{q=2}^{q=\infty}\frac{2rnB_q}{r^2n^2-q^2}\right)\cos\phi_r+\sum_{p=2}^{p=\infty}\frac{2pA_p}{r^2n^2-p^2}\sin\phi_r\right\} \quad (6)$$

Where there appear only even values of q and p and odd values of r and n.

Final Displacement

Suppose the charged particles pass through a second field identical with the first but with its center at a distance D from the origin. Consider the particle having the velocity $v_0=2av/n$ which passed the origin when the phase of the rth harmonic was ϕ_r. It passes D when the phase of this harmonic is ϕ_r'. Since it traveled parallel to the x-axis between fields its final displacement is

$$Y_f=\frac{n^2e}{4\pi mv^2}\sum_{r=1}^{r=\infty}C_r\left\{-\left(\frac{B_0}{rn}+\sum_{q=2}^{q=\infty}\frac{2rnB_q}{r^2n^2-q^2}\right)(\cos\phi_r+\cos\phi_r')+\sum_{p=2}^{p=\infty}\frac{2pA_p}{r^2n^2-p^2}(\sin\phi_r+\sin\phi_r')\right\}$$

For the rth harmonic this will be zero if $\phi_r'=\pi s_r+\phi_r$ where s_r is any odd integer. This condition is satisfied if $D=s_ra/rn$. We can choose $s_r=rs$ where s is an odd integer and it will then be satisfied for all odd harmonics at once since

$$D=rsa/rn=sa/n \quad (7)$$

Other Velocities Transmitted

Certain other velocities will also be transmitted for, with a given setting, $D/a=s/n=k$ and if any other odd integers, m and p, can be found such that $k=m/p$ then the corresponding velocity, $v=2av/p$ will pass. If s and n are incommensurable then p must be an odd multiple of s so that the other velocities which pass the filter will be $v'=v/h$ where h is an odd integer. These velocities are all less than v. If the alternating field is sufficiently strong so that the spread of the velocity between the fields is the maximum permitted by diaphrams in the apparatus then any lower velocity v' will generally have a wider spread and be cut out partially by the diaphrams.

Velocities Differing Slightly from v_0

We will now find the displacement of a particle with the velocity $v=v_0+\Delta v$ at a distance d beyond the end of the second field. Since the easiest experimental arrangement makes $f(x)=f(-x)$ we will consider this case, leaving only cosine terms in our Fouriers Series. If the time of passage from $x=a$ to $x=D+a$ is τ_1 and the time from $x=D+a$ to

$x=D+a+d$ is τ_2; if the y velocity component on leaving the first field is $(dy/dt)_1$ and on leaving the second field it is $(dy/dt)_2$ and if the displacement in the first field is y_1 and in the second y_2; then the displacement when $x=D+a+d$ is

$$y'=\tau_1(dy/dt)_1+y_1+y_2+\tau_2(dy/dt)_2=y_0+y_1+y_2+y_3$$

Starting with Eq. (2), expanding trigonometric functions in terms of the small angles $\Delta v/v_0$, neglecting powers of $\Delta v/v_0$ higher than the second and neglecting $\Delta v/v_0$ compared with one in the coefficient of q we obtain y_0. By a somewhat similar procedure, starting with Eq. (5) we obtain y_1 and y_2. We get y_4 in a manner similar to y_0. Adding the results gives

$$y'=\frac{nes}{4mv^2}\sum_{r=1}^{r=\infty}C_r\left\{\begin{aligned}&B_0\left[\left(\frac{r\pi(2n-s+2nd/a)}{2}\cos\phi_r-3\sin\phi_r\right)\left(\frac{\Delta v}{v_0}\right)^2\right.\\&\left.+2\sin\phi_r\left(\frac{\Delta v}{v_0}\right)\right]\\&+\sum_{q=2}^{q=\infty}\frac{2r^2n^2B_q}{r^2n^2-q^2}\left[\left(\frac{-3r^2n^2+5q^2}{r^2n^2-q^2}\cdot\sin\phi_r\right.\right.\\&\left.\left.+\frac{r\pi(2n-s+2nd/a)}{2}\cos\phi_r\right)\left(\frac{\Delta v}{v_0}\right)^2+2\sin\phi_r\left(\frac{\Delta v}{v_0}\right)\right]\end{aligned}\right\}$$

Since $(\Delta v/v_0)^2$ is very small the $(\Delta v/v_0)^2$ term is negligible except when $\sin\phi_r$ is of the order of $(\Delta v/v_0)$. In this case the $\sin\phi_r$ term in the coefficient of $(\Delta v/v_0)^2$ may be neglected since it is of the order of $(\Delta v/v_0)^3$, so we have finally

$$y'=\frac{nes}{4mv^2}\sum_{r=1}^{r=\infty}C_r\left[\left(B_0+\sum_{q=2}^{q=\infty}\frac{2r^2n^2B_q}{r^2n^2-q^2}\right)\left(\frac{r\pi(2n-s+2nd/a)}{2}\cos\phi_r\left(\frac{\Delta v}{v_0}\right)^2\right.\right.$$
$$\left.\left.+2\sin\phi_r\left(\frac{\Delta v}{v_0}\right)\right)\right] \tag{8}$$

In our further considerations we will assume that only the fundamental or one of the harmonics is present. In this case Eq. (8) takes the form

$$y'=\frac{Anes}{4mv^2}\left(B_0+\sum_{q=2}^{q=\infty}\frac{2r^2n^2B_q}{r^2n^2-q^2}\right)\left(\frac{r\pi(2n-s+2nd/a)}{2}\cos\phi\left(\frac{\Delta v}{v_0}\right)^2\right.$$
$$\left.+2\sin\phi\left(\frac{\Delta v}{v_0}\right)\right) \tag{8'}$$

where A is the maximum value of the field. From Eq. (6) we know that the maximum width of the beam between the fields is

$$W=2Y_{\max}=\frac{Anes}{4mv^2}\frac{2}{\pi rs}\left(B_0+\sum_{q=2}^{q=\infty}\frac{2r^2n^2B_q}{r^2n^2-q^2}\right) \tag{9}$$

Substituting this value in (8′) gives

$$y'=\frac{Wsr\pi}{2}\left(\frac{r\pi(2n-s+2nd/a)}{2}\cos\phi\left(\frac{\Delta v}{v_0}\right)^2+2\sin\phi\left(\frac{\Delta v}{v_0}\right)\right) \tag{10}$$

Intensity Considerations

In practice the beam will not be confined to the infinitely narrow X-axis but will have a finite width y_0. Hence there will be in the emergent beam, which we will also confine by a slit to a width y_0 along the x-axis, a certain distribution about the velocity v_0. For an apparatus of given dimensions we may compute the relative number which will emerge with any velocity $v=v_0+\Delta v$. Let y_0 be the width of the slit, i.e. the maximum value which y' can have and pass. Make the substitutions

$$\frac{\Delta v}{v_0}=\frac{y_0}{Wsr\pi}\sqrt{\frac{-1+\sqrt{1+4R^2\psi^2}}{2R^2}} \text{ where } R=\frac{(2n-s+2nd/a)y_0}{4Ws}$$

then Eq. (10) becomes

$$y'/y_0=R\left(\frac{-1+\sqrt{1+4R^2\psi^2}}{2R^2}\right)\cos\phi+\sqrt{\frac{-1+\sqrt{1+4R^2\psi^2}}{2R^2}}\sin\phi \tag{11}$$

Let $\tan\theta=(1/\sqrt{2})\sqrt{-1+\sqrt{1+4R^2\psi^2}}$ and this takes the form

$$y'/y_0=\psi\sin(\phi+\theta) \tag{12}$$

The displacement y' is always a maximum when $\sin(\phi+\theta)=1$. When this maximum is less than y_0 all values of ϕ contribute to the emergent intensity, but when it exceeds y_0 only certain values of ϕ contribute. The point where this change occurs is

$$\psi_m=\pm 1 \text{ or } \left(\frac{\Delta v}{v_0}\right)_m=\pm\frac{y_0}{Wsr\pi}\sqrt{\frac{-1+\sqrt{1+4R^2}}{2R^2}} \tag{13}$$

If I_0 is the intensity of the transmitted beam of particles with the velocity $v_0=2av/n$, then the intensity of any other value of $\Delta v/v_0$ and ϕ will be

$$I_{(\Delta v/v_0,\phi)}=\frac{y_0-|y'|}{y_0}I_0=\left(1-\frac{|y'|}{y_0}\right)I_0$$

Where $|y'|$ is the absolute value of the displacement for a given $\Delta v/v_0$ and ϕ. It is assumed that the entering beam is equally intense in all velocities and phases but enters parallel to the x-axis. $I_{(\Delta v/v_0,\,\phi)}$ is zero when $|y'|/y_0>1$. To get the value of $I_{(\Delta v/v_0)}$ we must sum up for all values of ϕ which permit that value of $\Delta v/v_0$ to pass the filter. From Eq. (13) all values of ϕ contribute when $\psi \leqq 1$. The expression for $I_{(\Delta v/v_0)}$ in this region is then

$$I_{(\Delta v/v_0)}=\frac{I_0}{\pi}\int_{-\theta}^{\pi-\theta}(1-|\psi\sin(\phi+\theta)|)d\phi=\left(1-\frac{2|\psi|}{\pi}\right)I_0 \qquad (14)$$

When $\psi \geqq 1$ only values of ϕ from $-\theta$ to ϕ_1 and from $\pi-2\theta-\phi_1$ to $\pi-\theta$ contribute. Here ϕ_1 has the value $\phi=\sin^{-1}(1/\psi)-\theta$ so that

$$I_{(\Delta v/v_0)}=\frac{2I_0}{\pi}\int_{-\theta}^{\phi_1}(1-|\psi\sin(\phi+\theta)|)d\phi$$

$$=\frac{2}{\pi}\left(\sin^{-1}\frac{1}{\psi}-\psi\left(1-\sqrt{1-\frac{1}{\psi^2}}\right)\right)I_0 \qquad (15)$$

This expression can be expanded, giving

$$I=\frac{1}{\pi\psi}\left(1+\frac{1}{3\cdot 4}\frac{1}{\psi^2}+\frac{1\cdot 3}{4}\frac{1}{5\cdot 6}\frac{1}{\psi^4}+\frac{1\cdot 3\cdot 5}{4\cdot 6}\frac{1}{7\cdot 8}\frac{1}{\psi^6}+\cdots\right)I_0$$

$$=(\pi\psi)^{-1}(1+.0833\psi^{-2}+.0250\psi^{-4}+.0112\psi^{-6}+.0061\psi^{-8}+\cdots)I_0$$

From this a table of I/I_0 in terms of ψ can be computed.

ψ	0	.5	1.0	1.5	2.0	3.0	5.0	8.0	12.0
I/I_0	1.000	.682	.363	.221	.163	.107	.064	.040	.027

The value of $\Delta v/v_0$ corresponding to any of the above values of I/I_0 can now readily be found from

$$\frac{\Delta v}{v_0}=\frac{\pm y_0}{Wsr\pi}\sqrt{\frac{-1+\sqrt{1+4R^2\psi^2}}{2R^2}}=\frac{\pm y_0\psi}{Wsr\pi}\sqrt{1-R^2\psi^2+\cdots}$$

In most cases R can be neglected. At least it can be considered constant for a given apparatus in which the ratio a/D does not vary greatly and the second slit is at the end of the second field ($d=0$) for then

$$R=\frac{(2n-s+2nd/a)y_0}{4Ws}=\frac{(2a/D-1)y_0}{4W}$$

D, a, y_0 and W are all dimensions in the apparatus. If R is neglected $\Delta v/v_0$ can be computed from the formula

$$\frac{\Delta v}{v_0}=\frac{y_0\psi}{W s\pi} \tag{16}$$

The distribution of velocities emerging, computed from Eqs. (14), (15) and (16) are shown in Fig. 2. The dimensions of the apparatus now set up are used. These are $a=4.9$ cms, $D=24.5$ cms to 27.5 cms, $y_0=.02$ cms and $W=.3$ cms. The ordinates represent the relative intensity and each abscissa scale gives the corresponding value of $\Delta v/v_0$ when the n is chosen as indicated in the vertical column of figures.

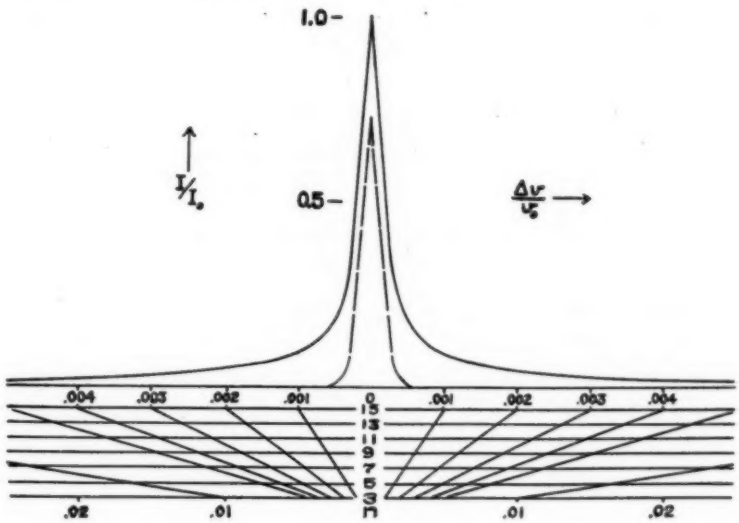

Fig. 2.

We have assumed heretofore that the entire beam of width W is permitted to pass between the two fields. An increase in resolving power with only a small loss in intensity can be obtained by cutting off the outer edges of this beam with a diaphram. If the width passed is W_0 we can see from Eqs. (6) and (9) that those particles which enter in the phase ϕ will be eliminated if $W_0/W<\cos\phi<1$. The effect of this on the intensity distribution curve can be found by modifying Eqs. (14) and (15). We neglect R (and hence θ) and let $\cos\phi_0=W_0/W$ so that when $\psi\leqq 1$ we have instead of Eq. (14):

$$I=\frac{I_0}{\pi}\int_{\phi_0}^{\pi-\phi_0}(1-|\psi\sin\phi|)d\phi=\left(1-\frac{2}{\pi}\left(\cos^{-1}\frac{W_0}{W}+\frac{|\psi|W_0}{W}\right)\right)I_0 \tag{17}$$

When $1 \leqq \psi \leqq 1/\sqrt{1-(W_0/W)^2}$ we have instead of Eq. (15):

$$I = \frac{2I_0}{\pi}\int_{\phi_0}^{\phi_1} (1 - |\psi \sin\phi|)d\phi$$

$$= \frac{2}{\pi}\left(\sin^{-1}\frac{1}{\psi} - \cos^{-1}\frac{W_0}{W} + \psi\left(\sqrt{1-\frac{1}{\psi^2}} - \frac{W_0}{W}\right)\right)I_0 \qquad (18)$$

When $1/\sqrt{1-(W_0/W)^2} \leqq \psi$, $I = 0$.

The distribution curve obtained by letting $W_0/W = .9$ is shown by the broken curve in Fig. 2.

If the above dimensions are used and the frequency applied is $\nu = 3\times10^{-6}$ 1/sec, corresponding to a radio wave-length of 100 meters, we can cover the following voltage ranges of positive rays by choosing proper values of n as shown.

n	Positive ray with velocity v_0				
1	437 volt	H^+	to	1748 volt	He^+
3	193 "	He^+	to	770 "	0^+
5	208 "	C^+	to	781 "	Sc^+
7	204 "	Na^+	to	753 "	Rb^+
9	208 "	K^+	to	737 "	Ba^+
11	209 "	Ni^+	to	750 "	Bi^+
13	203 "	Br^+	to	612 "	U^+
15	206 "	Ag^+	to	458 "	U^+

For a given choice of n the alternating potential used to obtain the theoretical distribution will be proportional to the accelerating potential required to give the charged particles the velocity v_0. The factor of proportionality can only be found experimentally since the form of $f(x)$ is unknown.

The chief source of error in the above theory lies in the assumption that "the field is everywhere perpendicular to the x-axis." Clearly this can only be strictly true along the axis itself. At other points there will be a longitudinal component retarding or accelerating the particle along the x-axis. The actual computation of this effect involves assumptions as to the nature of the field which are uncertain and depend on the individual apparatus. If the curvature of the field is sufficiently great the velocity with which a particle leaves the first field parallel to the x-axis will vary appreciably from v_0 for those values of the phase which correspond to large displacements. Only those particles which have the velocity v_0 will reach the second field in the correct phase to reverse the displacement and thus pass the slit. Also, in general, those particles which do not travel between fields parallel to the x-axis will be lost. Therefore, the chief effect of the curvature of the field, will be to weaken

the intensity of the emergent beam rather than to destroy its purity. Similar considerations hold for most of the accidental errors such as irregularities in the dimensions or positions of condensers, errors in the setting of D and so forth.

II. Experimental Arrangement

The experimental set up required to meet the conditions of the theory is obvious. We must apply an alternating potential of frequency ν to four condensers in parallel. These four will be grouped in two pairs. In each pair the distance between the centers of the condensers is a, and the distance between the pairs, center to center, is D. We must put the condensers plates far enough apart so that the curvature of the lines of force in the region used is negligible. All condensers must be of identical construction and must be placed in identical chambers in which are suitable apertures to permit the beam to pass through. Since it is desirable to be able to use different values of n for different regions the distance D should be adjustable.

III. Applications of the Velocity Filter

The more obvious applications of the velocity filter are:

1. It can be used instead of a magnetic field to analyze the velocities in a beam of similarly charged particles of equal mass.

2. It can be used to determine the relative masses present in a stream of similarly charged atoms or molecules which have fallen through the same potential.

3. Combined with electrostatic or magnetic deflection methods it can be used to find the masses of the constituents of a stream of positive rays containing all masses and all velocities. For precision work this possesses certain decided advantages to be discussed later.

The second application mentioned above has already proved successful. Dr. Klein, in this laboratory, completed last fall a velocity filter which he uses to identify the positive ions from the various thermionic emitters with which he works in his study of the secondary electron emission from positive ion bombardment. He varies the frequency applied to the filter until a maximum current passes through. A wavemeter and a voltmeter reading give the frequency and the accelerating potential and e/m is easily computed. The method seems quite convenient and accurate, the apparatus working successfully at the first trial.

Dr. Mattauch and the author have just set up a filter of higher resolving power which may be used as the one just mentioned or as in application three above. In the latter case it sorts out one velocity from a

heterogeneous beam of positive rays. The frequency determining the set of possible velocities can be kept constant with a piezoelectric oscillator. We may attach to the filter a magnetic or electrostatic analyzing device. Magnetic analysis will be used where a photographic record is desirable as in exploring work. We deflect our beam in a semicircle by means of a magnet with semidisk polepieces 25 cm in diameter, receiving them on a photographic plate. If positive ions are to make much impression on a photographic plate they must have a velocity of 5000 volts or greater. This would require an inconveniently high frequency on the filter and also, for heavy ions, a prohibitively powerful magnet. The difficulty is solved by applying 15,000 or 20,000 volts accelerating field immediately in front of the plate. At this point all particles, having completed a semicircle, are traveling parallel to each other and at right angles to the photographic plate, so a symmetrical accelerating field produces no distortion. It is unnecessary that this field be constant. The displacements on the plate are proportional to the radii of curvature in the magnetic field and these are directly proportional to the masses, since the velocity is constant. Thus we have a rigorously linear mass scale. All factors affect the image symmetrically so there is nothing to produce a relative shift between mass lines except inhomogeneities in the polepieces. The latter are of soft annealed steel run far below saturation and irregularities should be very small if they exist at all. They can be determined by comparing with the electrostatic method to be described next.

The electrostatic method may prove more satisfactory than the above for accurate work. The positive rays after passing the filter are deflected between two curved plates two mm apart and caught in a Faraday cylinder connected with an electrometer. Only a small range of masses passes between the plates with a given field but by altering the field successive masses are brought on the slit. The masses are directly proportional to the potential difference applied to the plates and can be compared as accurately as the potentials can be measured. All masses can be checked directly against oxygen, we hope with great precision, and our computations indicate that we should be able to determine the masses of most atoms within one hundredth of a unit of atomic weight. Such determinations would be of considerable interest in atomic theory.

The author wishes to thank Dr. Bowen for valuable suggestions and Professor Epstein for checking some of the equations.

California Institute of Technology,
July 16, 1926.

STUDIES IN THE ELECTRIFICATION OF DUST CLOUDS*

By V. E. Whitman

Abstract

Dust clouds were formed by blowing various pure chemical substances through tubes and the net electric charge imparted was determined as a function of the composition of the dust, tube material, area of contact between dust and tube during blowing process, velocity with which the dust moved through the tube, and length of path of the dust through the tube. An apparatus is described with which photographic records of the paths of particles in an electric field were obtained. Such photographs show the presence of positive, negative, and neutral particles in all dust clouds, even of very pure substances. The ratio of positive to negative electrification in a cloud is found to change as the larger particles in the cloud settle out but evidence is obtained which contradicts the hypothesis that the large particles carry an opposite charge from the small particles in a given cloud. The paper closes with a few remarks bearing on the relation of the present experimental data to the concept of a tribo-electric series.

I. Introduction

THE experimental work described in the following pages was done as part of a much larger program of the Bureau of Entomology, U. S. Department of Agriculture, concerned with the general study of the effect of static charges on the distribution and adherence of insecticides. That part of the above program which is described in this paper was conducted in the laboratories of the U. S. Bureau of Standards, in order to determine whether or not abnormally large charges could be imparted to particles in a dust cloud by a suitable choice of the material from which the cloud was blown. Although the results were negative from a practical point of view, they are considered interesting from a purely physical viewpoint as possibly adding something to our meager knowledge of the electrification of dust clouds in general.

II. Historical

Very little quantitative work has been published relative to the electrification assumed by dust particles when the latter are blown into the form of a cloud. In 1902, O. Knoblauch[1] investigated the charge remaining on a surface from which different substances fell as the surface was rotated about a horizontal axis. In the same article he put forth a

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[1] Knoblauch, Zeit. Phys. Chem. 39, 225 (1901).

theory which demanded that acids and acid salts should acquire a negative charge as they fell from the inverted surface; bases and basic salts should acquire a positive charge. This was consistent with his experimental findings.

In 1912–13–14 W. A. D. Rudge[2] published a series of articles on the electrification of artificial dust clouds. These experiments, when corrected as to the sign of electrification[3] lead to experimental laws in agreement with those demanded by Knoblauch's theory. Rudge was of the opinion that most of the particles in a cloud were of one sign, the opposite sign residing either on the air or on very fine dust particles.

A. Stäger[4] has carried this work forward recently from a slightly different angle, being primarily interested in explaining atmospheric phenomena. He describes experiments which led him to conclude that in any dust cloud, particles of both signs of electrification are present, the large and small particles being oppositely charged.

The investigation to be described in this paper was undertaken to determine the charge imparted to a dust cloud as a function of such controllable variables as the dust composition, the composition of the surface from which the dust was blown, and the relative velocity of the dust and the surface as the cloud was raised. It was also desired to determine how the charge on a dust cloud was distributed over the particles making up the cloud.

III. Apparatus

A. Cloud formation and electrometer. The apparatus used to form the clouds and measure the net charge upon them is shown diagrammatically in Fig. 1. The cloud material in the form of a fine powder was inserted as a small cylindrical slug into the right hand end of the tube A, which was carefully insulated from all grounded parts by the fused quartz pillar D. The slug of dust resting in the right hand end of A was approximately in the form of a cylinder filling the tube A completely for a short length. The method of inserting the slug was equivalent to placing a piston in the right hand end of the tube for about 5 mm, then placing A in a vertical position with the piston at the bottom, pouring the desired amount of dust into the top of A, tapping the tube so that the dust all went to the bottom and rested against the piston, and then carefully returning A to its horizontal position and withdrawing the piston. The left end of A projected through an opening into the wooden chamber B.

[2] Rudge, Phil. Mag. **23**, 852 (1912); **25**, 481 (1913).
[3] Rudge, Proc. Royal Soc. London **90**, 256 (1914).
[4] Stäger, Ann. d. Physik **76**, 49 (1925).

The fused quartz tube C was then inserted behind the slug of powder in A and a blast of air, of any desired pressure P, was released from the reservoir V when a cloud was desired. The dust was thus blown through A and into the box B where it formed a cloud which slowly settled under gravity into the particle polarity recorder at F. This part of the apparatus will be described in detail below. The process of cloud formation just described will hereafter be referred to as forming a cloud "through the tube A." Preliminary experiments showed that the presence of the box B had practically no effect on the phenomena observed.

Since repeated experiments showed that no charge was imparted to A by simply blowing dust-free air through it, the charge it acquired

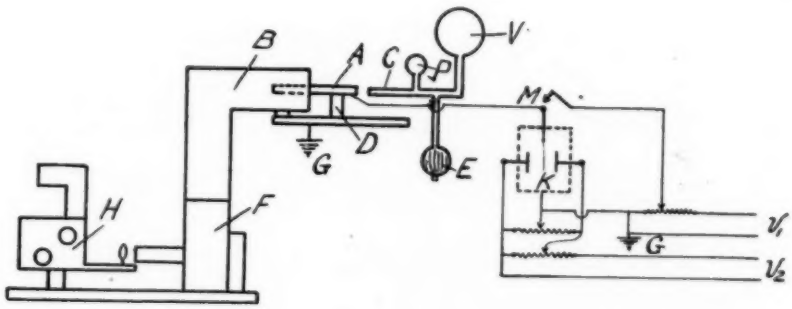


Fig. 1. Diagram of apparatus. A, metal tube through which dust cloud is formed; B, box in which cloud settles; C, quartz tube for directing blast of air through A; D, quartz post insulator; E, bulb for raising pressure of air; F, particle polarity recorder; G, ground connection; H, arc light; K, electrometer case; M, key used in calibrating electrometer; P, pressure gauge; V, air reservoir; v_1, source of voltage for calibrating electrometer; v^2, source of voltage for electrometer plates.

when a slug of dust was blown through it to form a cloud was necessarily equal and opposite to that residing on the cloud particles. This charge on A was measured by the electrometer shown at the right of Fig. 1. K is an Edelmann unifilar electrometer, v_2 the source of plate potential, and v_1 a source of calibrating potential which could be applied to the fibre through the key M.

It should be clearly recognized that electrometer readings with the apparatus described indicate only the "net" charge on the cloud as a whole and should not be interpreted as a measure of the charge associated with individual particles. An indication of the latter charge was made possible by the apparatus described below which will be referred to as a particle polarity recorder.

B. Particle polarity recorder. A photograph of this apparatus with part of the case removed is given in Fig. 2. The cloud of dust enters at

H and settles under gravity, part of it coming into the electric field F between the electrodes E_1, E_2. To photograph the particles in this field F, light from an arc at A was focused on a slit mounted at B. The image of the slit was focused at F by means of an $F:3.5$ lens at C and the prism D. The axis of the camera lens G was perpendicular to this beam of light so that light entered the camera only after reflection from particles.

As a cloud settled through F, the shutter of the camera was opened and a time exposure of about one second duration made. A Sept motion picture camera was used for this purpose, its original lens being replaced by a microscope objective installed as seen at G.

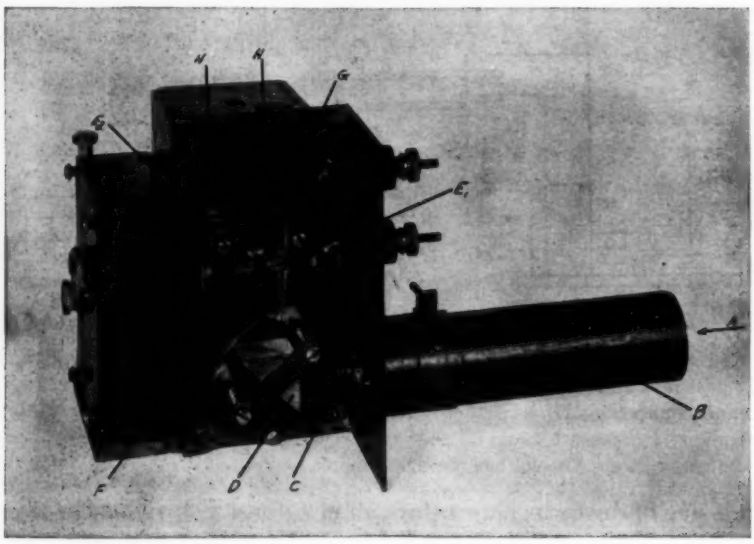
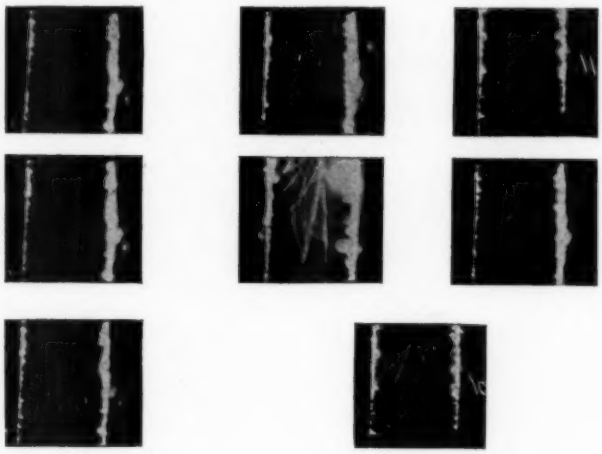


Fig. 2. Particle polarity recorder. A, direction of entrance of light from arc; B, tube containing optical slit system; C, lens to focus image of slit onto F; D, prism; E_1 E_2, electrodes; F, field between electrodes; G, lens of camera; H,H, direction of entrance of dust cloud.

With no difference of potential between E_1 and E_2, the photographs obtained showed straight streaks as seen in Fig. 3, A. When an electric field was established between E_1 and E_2 the particle paths took on the typical form seen in Fig. 3, B. The illustrations in Fig. 3 are typical photographs recorded by this apparatus.

Electrodes with chisel shaped ends, with the chisel edges vertical, as well as those with truncated cone ends, were tried, with no noticeable difference in the results.

In the interpretation of photographs taken with this apparatus, the streaks were taken to be the paths of neutral, positive or negative particles according as they went parallel to the electrodes, or sloped toward one electrode or the other. Such an interpretation is justified as follows: (1) The possibility of air currents causing particles to trace curved paths not parallel to the electrodes was ruled out by repeated experiments with no electrostatic field between the electrodes. Paths under such conditions are to be seen in Fig. 3, *A* as practically straight lines, parallel to the electrode surfaces. Aerodynamically, conditions at *B* and *A* of Fig. 3 were the same and therefore air currents could not have caused the curved paths noted. Moreover, the occasional appearance of



A B

Fig. 3. Sample photographs made with particle polarity recorder. *A*, particle paths with no electrostatic field between electrodes; *B*, particle paths with electrostatic field between electrodes.

straight paths parallel to the electrode surfaces as in Fig. 3, *B* makes it very improbable that air currents could be responsible for the majority of paths which are curved. (2) The possibility of the force exerted on a particle of high dielectric constant by a non-uniform electrostatic field causing path curvature is ruled out by evidence against it, also to be seen in Fig. 3, *B*, where some particles cross the center of the field to strike the opposite electrode, and still others fall undeviated, near and parallel to the electrode surfaces.

IV. Results

The substances used in this work were in the form of fine powders and were of the grade commercially known as "chemically pure."

Particles ranging in diameter from 0.1 mm down to sub-microscopic size were present in all clouds, but most of the particles present were of the order of 0.02 mm. Throughout the experiments, all carried out at room temperature, the samples of powder were in equilibrium with the atmosphere at about 50 percent humidity, except in some special runs using ground SiO_2 where the samples were carefully dried.

A. Electrometer measurements. A series of readings were first taken in order to determine the net sign of the electrification imparted to different dust clouds formed through various tubes. No attempt was made to make the readings quantitative. No special precautions were taken with the tubes through which these clouds were formed. The aluminum and copper tubes were used as obtained from the machine shop: the "platinum tube" consisted of a brass tube lined with platinum foil. The results are given in Table I.

TABLE I

Showing net sign on different clouds formed through different tubes

Cloud Material	Al tube	Cu tube	Pt tube	Cloud Material	Al tube	Cu tube	Pt tube
Se	−	−	−	As_2O_3	−	−	−
Al	−	−	+	ZnO	+	+	(*)
Zn	+	+	+	S	−	−	−
Bi_2O_3	−	−	−	SiO_2	−	−	−

(*) No measurements made.

For this random lot of substances used, the net sign on the cloud appears to be independent of the tube used except in the case of the aluminum dust. This aluminum dust was the commercial variety used as a pigment. It was repeatedly washed in ether before being used in this work in an effort to remove all traces of stearic acid, with which all such powders are coated.

These preliminary runs showed the great difficulty of obtaining readings which would check quantitatively. It was found necessary to use exactly the same amount of sample and to force it through the tube at the same velocity each time. These precautions led to values which could be reproduced sufficiently well for the work in hand. A change of sign was never noted in any series of readings. Most of the values recorded are an average of ten readings, and would be expected to deviate from the average of an infinite number of readings by less than 10 percent.

A series of experiments were conducted in which the mass of dust was held constant and the dependence of net charge on air pressure investigated. In Fig. 4, the unbroken curve was determined directly from experiment; the velocities plotted in the dotted curve were calcu-

lated from the observed pressures by assuming that the air at a given pressure served only to accelerate the mass of dust considered as a frictionless piston.

Although only one substance, ground fused quartz, was used in the experiments just described and summarized in Fig. 4, the shape of the curve plotted is not believed to be peculiar to any one material. The general form of the relationship sought should be independent of all variables except those plotted.

A few experiments were conducted which showed conclusively that the net charge acquired by a cloud resulting from a slug of given mass increased as the area of the surface over which the slug rubbed increased. The form of this relationship was not determined.

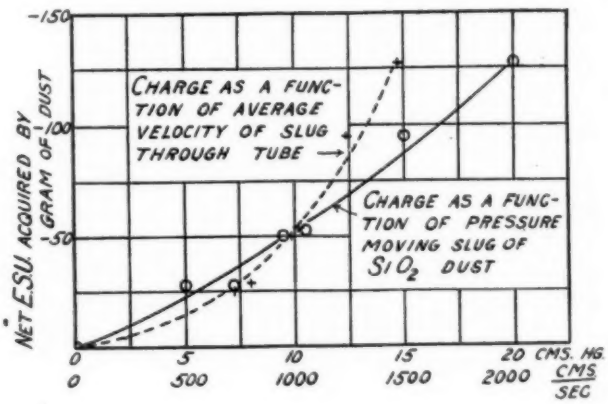


Fig. 4. Curves showing dependence of net charge on cloud upon the velocity with which the forming cloud rubs along the surface from which the cloud is blown.

The results of a series of runs conducted to determine quantitatively the net charge per gram acquired by equal volumes of different dusts as they were blown through the same tube are shown in Table II.

The above values were obtained when the clouds were formed through a brass tube whose inner surface had not been touched except by washing with alcohol. Its inner coating was therefore probably quite free from oil and grease but heavily oxidized. The values given under the heading "Electrification of cloud e.s.u. per gram" were calculated from the mass of material and the charge imparted to the tube with the assumption that the charge was directly proportional to the mass of dust used. This assumption was justified experimentally within the experimental error.

Although Rudge[2] had dismissed such a possibility, it now seemed evident that the net charge acquired by a cloud of dust should depend

upon the nature of the surface from which the cloud had been raised. Ground fused quartz, carefully dried, was chosen as the cloud material and blown through a number of different tubes. The insides of the aluminum, copper, brass, and steel tubes were carefully drilled and at the beginning and middle of each experiment were reamed and washed with alcohol. The Pt and Ni tubes were obtained by lining the inside of

TABLE II

Showing net charge acquired by tube and dust as clouds of different materials were formed through the same brass tube

Material	Borax	$NaHCO_3$	CaO	SiO_2	NH_4Cl	Na_2CO_3	NaF
Volume of material (cc)	.24	.24	.24	.24	.24	.24	.24
Mass of material (gms)	.15	.17	.07	.13	.19	.12	.13
Electrification of tube (e. s. u.)	+ 1.5	− 2.0	− 8.1	+11.5	+ 2.1	+ .1	− 5.9
Electrification of cloud (e. s. u. per gr.)	−10	+12	+115	−88	−11	−0.8	45

two brass tubes with thick foil of these two elements. The inside surfaces of these two tubes are believed to have been in substantially the same mechanical condition and practically free from oxide and grease.

The net charge on clouds of SiO_2 blown through these various tubes is given in Table III:

TABLE III

Showing net charge acquired by tube and dust as clouds of ground fused quartz were formed through tubes of different materials

Tube Material	Al	Cu	Pt	Steel	Ni	Brass
Mass of dust used. (gms)	.13	.13	.13	.13	.13	.13
Charge on Tube. (e. s. u.)	+78	+55	+89	+61	+54	+64
Electrification of cloud (e. s. u. per gr.)	−600	−425	−685	−470	−415	−495

The readings in Table III are averages of ten separate determinations, all slugs being of the same mass and forced through the same length of tube with the same air pressure and hence with the same velocity. The values given as "Electrification of cloud e.s.u. per gram of dust" were calculated, as in Table II on the assumption of a linear relation between mass and charge.

It will be noticed that the value of e.s.u. per gram for fused quartz blown through a brass tube is over five times as large in Table III as in Table II. This may be due either to the difference in surface of the two

brass tubes or to the difference in moisture content of the SiO_2 in the two experiments.

No other work was done to determine the effect of moisture content on electrification, although it was believed to be important as suggested by the effect of drying on the SiO_2 blown through the brass tube. The results given in this report are believed to be comparable among themselves, and refer, unless otherwise stated, to dust which had probably attained equilibrium with a room humidity which averaged about 50 percent.

B. Photographic Results. Photographs were taken with the apparatus described in Section III B, of clouds of different materials blown through the same brass tube as was used in obtaining Table II. These photographs were taken about one second after the air cock was opened, and a count of the traces left by different particles is given in Table IV. Each figure is an average based upon about seven separate exposures.

TABLE IV

Relative number of positive, negative, and neutral dust particles in different clouds

Cloud material	Borax	CaO	SiO_2	NH_4Cl	Na_2CO_3
(+) Average particles per exposure	2.1	2.7	1.4	0.7	1.0
(−) Average particles per exposure	3.9	2.0	2.4	1.8	1.4
Neutral Ave. particles per exposure	2.1	1.0	1.6	2.0	2.4

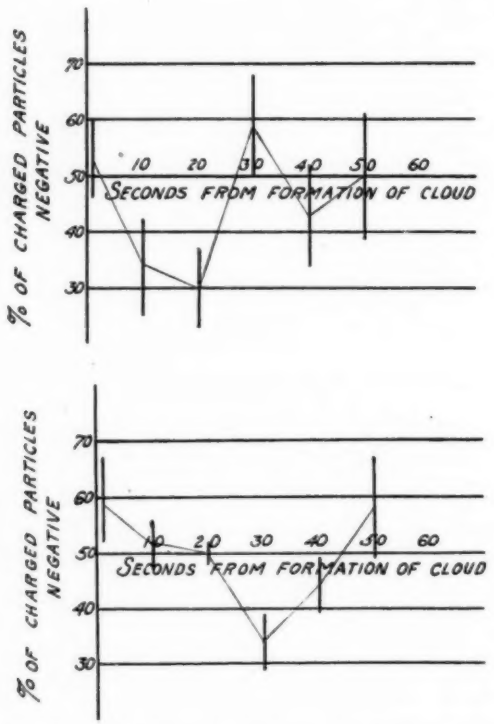
The slopes of the paths of both positive and negative particles in the same exposure were always so similar that it seemed necessary to conclude that they carried for the most part nearly equal opposite charges. It will be noticed that on this assumption, the sign of the net charge predicted for a cloud by Table IV is that found experimentally and recorded in Table II. The values given in Table II must therefore be regarded as net charges due only to the difference between two much larger opposing effects.

Some of Rudge's experiments suggested to him that the large and small particles in a dust cloud might be oppositely charged.[3] Stäger carried out some further experiments which led him also to conclude definitely that the small particles are oppositely charged from the large ones.[4] From the nature of Stäger's experiments, however, it was evident that he was measuring only a "net" charge, which, to be sure, he observed to change sign as the large particles in a cloud settled out.

It was therefore thought desirable to investigate this point with the particle polarity recorder. Two substances, Sulphur and SiO_2, were selected for the cloud materials and ten clouds were formed of each through a Pt tube. Photographs of charge distribution were taken at

$t=0$, 10, 20, 30, 40, and 50 seconds after the formation of the clouds. After this time had elapsed practically no more particles appeared in the field and no records were made. The sulphur was analyzed and found to be 99.99 percent pure rhombic. The quartz powder was of the same order of purity as the sulphur. Throughout the experiments both samples were kept in a dessicator until the small slug of material was inserted in the tube A.

The results given in Figs. 5 and 6 are averages for the ten clouds of each material. In both of these curves the vertical lines show the limits



Figs. 5 and 6. Curves showing the distribution of positive and negative charges among particles of different sizes.

within which the ordinates of the curve might vary from the mean. They show that the ratio of positive to negative electricity was in favor of the negative in that part of the cloud made up of the larger particles (i.e. those falling first). After these larger particles settled out, or as time elapsed, smaller particles which were found to be mostly positively charged came between the electrodes. This indicates that the net sign on that part of the cloud composed of particles of the size falling at this

time would have been positive although the net charge on a cloud of the larger particles would have been negative. Further examination of Figs. 5 and 6 shows that still smaller particles had a net negative charge again. Fig. 5 shows still a fourth group of very fine particles, falling 40 seconds after the cloud had been formed which had an excess of positive electrification. The accuracy of these measurements allows no great significance to be attached to the results. They show conclusively, however, that any general statement to the effect that the large particles in a cloud are oppositely charged from the small ones is incorrect. The results embodied in Figs. 5 and 6 also indicate the distribution of charge among different sizes of particles is not purely random.

It has already been mentioned that the positive and negative streaks in the same exposure had practically the same slopes, and therefore, for the same sized particles, carried the same numerical charge. In the runs from which Figs. 5 and 6 were plotted, the slopes of the paths did not change appreciably with time, or, what is the same thing, with particle size. This shows that, within the experimental error, the charge per particle was directly proportional to its mass.

From Stokes' law, the mass of a particle photographed at any instant is inversely proportional to the cube of the difference in time between that of cloud formation and that at which the exposure was made. Such a consideration, taken together with the actual number of particles photographed at any time, shows that less than 1/1000 of the mass of dust falling was photographed and counted after the first exposure. This, taken together with the conclusion of the previous paragraph, that charge per particle is proportional to the mass of the particle, shows that the net sign of a given cloud should be the same as that given by the first ($t=0$) point on curves such as Figs. 5 and 6. The agreement between Figs. 5 and 6 and Table I is therefore complete.

Although these results are not inconsistent with those of Stäger they give a decidedly different aspect to the mechanism by which the charges must have originated. They show that the size of the particle does not solely determine the sign of its electrification, there being charges of both signs present on all sizes of particles, although perhaps in different proportions. It was the net effect of this "proportion" factor that Stäger measured.

V. Discussion of Results

The usual statements concerning tribo-electric phenomena, and in particular, the description of results by the tribo-electric series[5] neces-

[5] P. W. Shaw, Roy. Soc. Proc. **94**, 16 (1917).

sarily implies that any substance when rubbed against another substance should receive a charge of perfectly definite sign, depending upon the relative position of the substances in the series. Such a concept precludes the possibility of opposite signs existing in a cloud of one pure substance blown from an equally pure material. H. F. Richards[6] has concluded from experiments conducted by him that, in general, tribo-electrification can be regarded as a superposition of two effects, one a contact electrification, and the other an inertia effect of mobile electrons. Richards states that these two effects may even be opposite in sign, citing as a possible example the anomalous behavior of mercury, which, when struck with a glass rod, becomes positively charged, but becomes negatively charged when rubbed with the rod. It is not probable, however, that the normal component of velocity in the experiments described in the present work was sufficiently large to give an inertia electrification of the same order of magnitude as that acquired by friction or contact. Knoblauch's theory,[1] which is consistent with the concept of a tribo-electric series, likewise fails to explain the signs existing in such a cloud.

A. Contamination possibilities. The present results on powdered chemical elements such as S in a Pt tube can not be accounted for by assuming either impure powder or a non-uniform surface. The order of the results observed is such that the chemical impurity of neither powder nor surface can explain them. Neither is it apparent that the observed effects could be expected to result from mere mechanical irregularities in the shape of the surface.

The experimental fact that the net charge acquired by the dust is dependent upon its chemical composition shows that any gas films present[7] must be penetrated during the process of electrification or else that the composition of the film must depend greatly on the chemical nature of the particle.

It is quite improbable that some particles of a given element are covered with impenetrable gas films while others are penetrated. Admitting such a possibility, the present theories could account for the results given here only if the tube material happened to occupy a place in the tribo-electric series somewhere between that of the particle material and that of the gas film. If all particles are coated with impenetrable films the situation becomes the same as with all films penetrable, except that the chemical composition of the active material (in this case the film) is now different from that of the core of the particle.

[6] Richards, Phys. Rev. **16**, 290 (1920); **22**, 122 (1923).

[7] Shaw and Gilbert, Proc. Phys. Loc. Lond. **37**, 195 (1925).

B. Crystallographic possibilities. It is very probable that the electrification of the observed clouds was a superposition of the following effects: first, an electrification due to the contact between the dust and the tube; second, an electrification due to contacts between different crystallographic faces of the small particles forming clouds. This second effect has been noted by Rudge in the case of large crystals; its action in clouds would lead to equal numbers of positive and negative particles while contributing zero to the net charge on the cloud. The net charge would then be affected solely by the first effect, the existence of which is proven by the dependence of net charge upon tube material. The existence of the second effect with its implied contact electric differences between different crystallographic faces of like crystals, logically demands that it should manifest itself in a more careful analysis of the first effect.

Any such analysis leads to the prediction of a distribution of charges too complicated to warrant consideration in connection with the present experimental data.

The photographs of particle paths, previously described, show that whatever effects are existent, they developed charges of substantially the same magnitude.

We can therefore explain the existence of particles of both signs in clouds of pure substances blown from clean surfaces, without recourse to any other than the classical contact potential theory if we admit that particles in a cloud can become charged either by contact with the clean surface, or by contact with the other particles, and if we further assume that charges developed by all types of contact are of the same order of magnitude.

C. Atomic possibilities. In the case of compounds, say SiO_2, sliding along a surface of an element x, charges of both signs might be expected on the dust particles in the special case in which x occupied a position in the tribo-electric series intermediate between Si and O; in this event, a Si atom rubbing along x might get an opposite charge from that acquired by a particle if one of its O corners happened to come into contact with x.

The experiments described herein seem to show that such a special position of the surface x in the tribo-electric series is not necessary. Dust clouds of all of the powders tried when raised from any of the surfaces were found to contain particles of both signs.

It is possible to formulate a theory which will account for the presence of an excess or deficiency of a few electrons per particle if it is assumed that (1) the transfer of an electron can take place when two atoms are sufficiently close for two electrons to be shared by orbits in both atoms,

and (2) at the instant of separation, the decision as to where the electrons go depends in part upon the geometry of the contact and partly upon the chemical nature of the separate atoms (probably as evidenced by their photo-electric work functions). Since the configuration of such atomic "contacts" at the instant of separation might be any one of a great number, the transfer of electrons in such a mechanism would be subject to the laws of probability, making the appearance of particles of either sign possible. The effect of the photo-electric work functions in such a concept would be to so distort the probability curve that an excess of particles of one sign of electrification would in general predominate.

Although such a theory, based on probability considerations, seems to be consistent with the appearance of particles with an excess or deficiency of one or two electrons, it, however, seems to demand a very high order of improbability in order to account for the appearance of charges corresponding to a larger number of electrons.[8]

From data obtained in this work and from any one of several assumptions, which, while necessarily rough, seem to be fairly probable, it can be calculated that the charge per particle in these experiments quite often exceeded 20 electrons.

VI. Conclusions

1. When powders are blown into dust clouds, some of the particles in the resulting cloud are positively charged, some negatively charged, and some neutral. This presence of both signs of electrification on clouds of pure substances is not accounted for by the usual theories of frictional and contact electrification.

2. The present investigation indicates the presence of particles of both signs, regardless of particle size. In a dust cloud, the large particles carry most of the charge.

3. The electrometer methods of measurement employed by Rudge and Stäger measure the net charge on a cloud as a whole and therefore can not be interpreted as measuring the charge associated with individual particles. The net charge on any cloud depends both upon the chemical nature of the cloud material and that of the surface from which the cloud is blown. The net charge may depend upon the physical nature of the dust and upon the surface from which it is blown. The net charge depends upon the area of "contact" between the dust and the surface from which it is blown. The net charge increases with either the velocity or pressure at this contact, or both.

[8] Czüber, Wahrscheinlichkeitsrechnung **1**, 184 (1908).

The present investigation has impressed the author with the importance of controlling and measuring humidity in any further work of this nature. The work of investigating electric charges arising at solid-solid interfaces has now reached a stage where it should be transferred to a vacuum "machine shop" as used by Millikan. The most important of the heretofore uncontrolled variables might then be fixed and the results interpreted accordingly.

In conclusion, the author wishes to express his indebtedness to Dr. F. B. Silsbee for his interest and many helpful suggestions throughout the course of these experiments.

DEPARTMENT OF COMMERCE,
BUREAU OF STANDARDS,
WASHINGTON, D. C.
July 19, 1926.

TORQUE ON REVOLVING CYLINDRICAL MAGNET

By A. L. Kimball, Jr.

Abstract

In a recent article Zeleny and Page have shown that the torque on a revolving cylindrical magnet, with a side arm dipping into a mercury trough, consisted of two parts: namely, a torque arising from a reaction between the current in the side arm, and the external magnetic field, and a torque produced by the reaction between the current flowing in the magnet and the flux within the magnet. In the following paper the torque is considered as arising from the reaction between the external circuit and the external field. From the viewpoint of the electrical engineer, this is the better way of looking at the problem because it involves the conception of a reaction between a magnetic field revolving with the rotor and a fixed external circuit, which is in conformity with the usual method of analysis of rotating electrical machinery. A detailed analysis is given from this point of view which gives a value for the torque identical with that of Zeleny and Page. That there must be such an agreement can also be shown from general considerations, such as from the law of action and reaction, or from considerations of flux linkage.

IN A recent number of this magazine[1] attention was called to the fact that the usual explanations of the cause of the electromagnetic rotation of a vertical cylindrical bar magnet carrying a side arm (Fig. 1) which dips into a circular trough of mercury were incorrect. An analysis of the problem was given—the results of which were experimentally verified. The viewpoint which was taken in the theory developed was that the torque which is produced arises from a reaction between the flux and current, both of which are carried by the magnet, involving the necessity of thinking of the flux carried by the magnet as fixed to outside space.

While this method of analysis gives the correct result, there is another way of looking at the problem—suggested by Mr. E. H. Hull, of this laboratory—which does not involve the necessity of considering a flux fixed to outside space. If the flux be thought of as fixed to the magnet and revolving with it, no torque can be produced by the current in the magnet or that in the cross arm, because, since both the current and the flux are "fixed" to the magnet, and the reactions between them are equal and opposite, they must balance out. The torque on the magnet then comes entirely from the reaction between the external flux of the magnet and the fixed external circuit which is not carried by the magnet. This is the better way of looking at the problem from the view point of the

[1] Zeleny and Page, Phys. Rev. **24**, 544 (1924).

electrical engineer because it brings the problem into conformity with the usual methods of analysis of rotating electrical machinery, wherein the flux is thought of as fixed to the armature, and the reaction which produces the torque as coming entirely from the external flux of the magnet and the fixed external circuit.

Although it can be shown from the law of action and reaction, or from considerations of flux linkage, that the torque must be the same whether

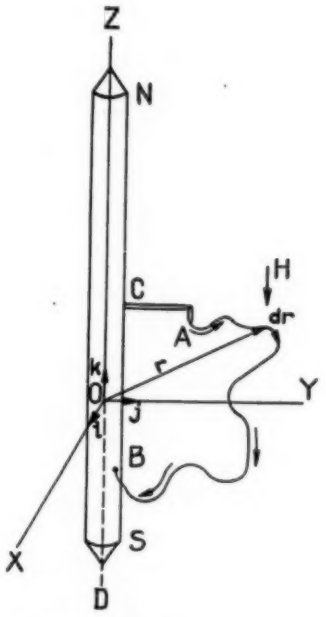


Fig. 1. Diagram of magnet showing where the current leaves the end of the side arm at A, passes through any external circuit, and enters the magnet at B.

calculated on the basis of the reaction upon the internal or the external portion of the electrical circuit, a direct calculation of the torque from the viewpoint of the reaction upon the external portion of the circuit is of interest.

In the following discussion the magnitude of the torque is calculated on this basis using the Biot-Savart law for the electro magnetic reaction on an element of electric current in a magnetic field.

Consider an external circuit AB, Fig. 1, which may follow any path between the points A and B where it leaves and enters the magnet, this circuit containing the source of voltage used to drive the current. Consider an element $d\boldsymbol{r}$ of this circuit in the external magnetic field of strength $\boldsymbol{H}$. The force $d\boldsymbol{F}$ on this element is equal to

$$-I\boldsymbol{H}\times d\boldsymbol{r}. \tag{1}$$

Its moment about the origin O on the axis of the magnet is equal to

$$\boldsymbol{r}\times d\boldsymbol{F} \tag{2}$$

The scalar magnitude of its component along the Z-axis is equal to

$$\begin{aligned} dL &= \boldsymbol{k}\cdot(\boldsymbol{r}\times d\boldsymbol{F}) \\ &= (\boldsymbol{k}\times\boldsymbol{r})\cdot d\boldsymbol{F} \end{aligned} \tag{3}$$

where $\boldsymbol{k}$ is the unit vector along the Z-axis.

Substituting the value of $d\boldsymbol{F}$ given in (1)

$$dL = I(\boldsymbol{k}\times\boldsymbol{r})\cdot(\boldsymbol{H}\times d\boldsymbol{r}) \tag{4}$$

in scalar magnitude, dropping the minus sign. By an interchange of dot and cross, this expression becomes

$$dL = I(\boldsymbol{k}\times\boldsymbol{r})\times\boldsymbol{H}\cdot d\boldsymbol{r} \tag{5}$$

Thus

$$\begin{aligned} L &= \int_A^B I(\boldsymbol{k}\times\boldsymbol{r})\times\boldsymbol{H}\cdot d\boldsymbol{r} \\ &= I\int_A^B \boldsymbol{R}\cdot d\boldsymbol{r} \end{aligned} \tag{6}$$

(where the vector $(\boldsymbol{k}\times\boldsymbol{r})\times\boldsymbol{H}$ is signified by $\boldsymbol{R}$) represents the total moment of the forces on the circuit about the axis of the magnet, or from the law of equal action and reaction it equals the torque on the magnet about its axis. This is seen to be the product of I into the line integral of the vector $(\boldsymbol{k}\times\boldsymbol{r})\times\boldsymbol{H}=\boldsymbol{R}$ along the electric circuit from A to B. It will be shown that the value of this integral depends only upon its limits, so that the torque is the same for any path which may be taken by the electric circuit from A to B, and the torque can then easily be calculated for certain cases.

For the integral (6) to be dependent upon its limits only, the quantity $d\psi=\boldsymbol{R}\cdot d\boldsymbol{r}$ must be an exact differential. The condition that $d\psi$ be an exact differential is

$$\nabla\times\boldsymbol{R}=0 \tag{7}$$

or in words that the curl of the vector $\boldsymbol{R}$ vanish.

Expressing the vector $\boldsymbol{R}=(\boldsymbol{k}\times\boldsymbol{r})\times\boldsymbol{H}$ in terms of its components by substituting $\boldsymbol{r}=ix+jy+kz$ and $\boldsymbol{H}=iH_x+jH_y+kH_z$ and reducing

$$\boldsymbol{R}=i\boldsymbol{H}_x x+j\boldsymbol{H}_y y-k(\boldsymbol{H}_x x+\boldsymbol{H}_y y) \tag{8}$$

$\boldsymbol{H}$ is derived from a potential function which will be called ϕ. The curl of $\boldsymbol{H}$ is equal to zero, such that

$$\boldsymbol{H}_x=\partial\phi/\partial x\ ;\ \boldsymbol{H}_y=\partial\phi/\partial y\ ;\ \boldsymbol{H}_z=\partial\phi/\partial z. \tag{9}$$

From (8) and (9)

$$R_x=x\partial\phi/\partial z\ ;\ R_y=y\partial\phi/\partial z\ ;\ R_z=-(x\partial\phi/\partial x+y\partial\phi/dy) \tag{10}$$

Using these values for the components of R and making use of Eq. (10) and also remembering that for constant torque the flux is symmetrically distributed about the magnet such that

$$x\partial\phi/\partial y=y\partial\phi/\partial x$$

the condition (7) is found to be satisfied. The torque represented by the integral (6) therefore depends upon the position of the ends of the external circuit only, and not on the path of this circuit.

In finding the torque, the circuit between A and B then can be placed where most convenient for calculation.

Imagine the flux line which passes through A and that which passes through B each to be revolved about the axes of the magnet, thus describing a pair of coaxial surfaces of revolution, on one of which lies the point A and the other the point B. From a consideration of the Biot-Savart law, as expressed by Eq. (1), when part of the electric circuit lies on one of these surfaces of revolution no torque can arise, because the magnetic force on each element of this part of the circuit is always normal to the surface. Therefore a convenient circuit to use between A and B in calculating the torque is one which goes from the surface of revolution containing A to that containing B by a perpendicular path. The remainder of the circuit is taken on the surfaces of revolution and this contributes nothing to the torque.

An examination of the integral (6) reveals the fact that the vector $(\boldsymbol{k}\times\boldsymbol{r})\times\boldsymbol{H}$ is perpendicular to the surfaces of revolution. Therefore, if the integration is performed along the direction of this vector, perpendicular to those surfaces, the integral may be expressed as a scalar integral, or

$$L=I\int_A^B aH\,dr \tag{11}$$

where a = the length of the radius drawn perpendicularly from the axis of the magnet to the element dr.

This integral can be expressed in terms of the flux passing between the two surfaces of revolution on which A and B lie.

The rate of change with respect to r of flux contained within such a surface in a direction perpendicular to these surfaces is

$$d\phi/dr = 2\pi aH$$

or

$$aH dr = d\phi/2\pi \tag{12}$$

Substituting (12) in (11)

$$L = I\int_A^B d\phi/2\pi = I(N_B - N_A)/2\pi \tag{13}$$

where the integration is performed between the surfaces of revolution on which A and B lie, and N_A is the total flux enclosed inside of the A surface and N_B that within the B surface.

This expression is seen to check the one given by Zeleny and Page.

Another way to solve this problem from the external circuit viewpoint is to extend the current sheet idea of Zeleny and Page, regarding the circuit from A to B, of Fig. 1 as a special case of a dissymmetrical current sheet flowing in the symmetrical external field. By substituting $\boldsymbol{H}$ for $\boldsymbol{B}$ and integrating the flux between concentric rings passing through A and B as limits, the same expression for the torque is arrived at.

A physical picture of the problem which appeals to some minds can be obtained by remembering that torque is equal to the work per radian of rotation and thinking of the work done in terms of the number of magnetic lines of force cut by the fixed external circuit when the magnet with its field fixed to it is rotated through one radian. If the circuit is in form of a closed loop and the field is symmetrical, evidently the resultant number of lines of force cut is zero. If the external circuit goes from A and B along any path the number of lines cut per radian of rotation is the total number passing through the anular band surrounding the magnet and whose edges pass through A and B, divided by 2π, i.e. $(N_B - N_A/2\pi$ and since the work done (per radian) is equal to the number of lines cut times the current,

$$L = I(N_B - N_A)/2\pi$$

which agrees with the values given previously. Simple geometrical considerations make it clear that the lines of force cut by the open circuit depend only upon the positions of A and B in the field.

An experiment was tried in which a cobalt steel magnet was suspended vertically in a conducting sheath in which the magnet was fixed but from which it was electrically insulated. The magnet was suspended on a 7 mil tungsten wire whose elastic coefficient was found by oscillation measurements using a mass of known moment of inertia. The angular deflections were observed by the deflections of a spot of light reflected from a small mirror. This experiment was tried to see if any difference

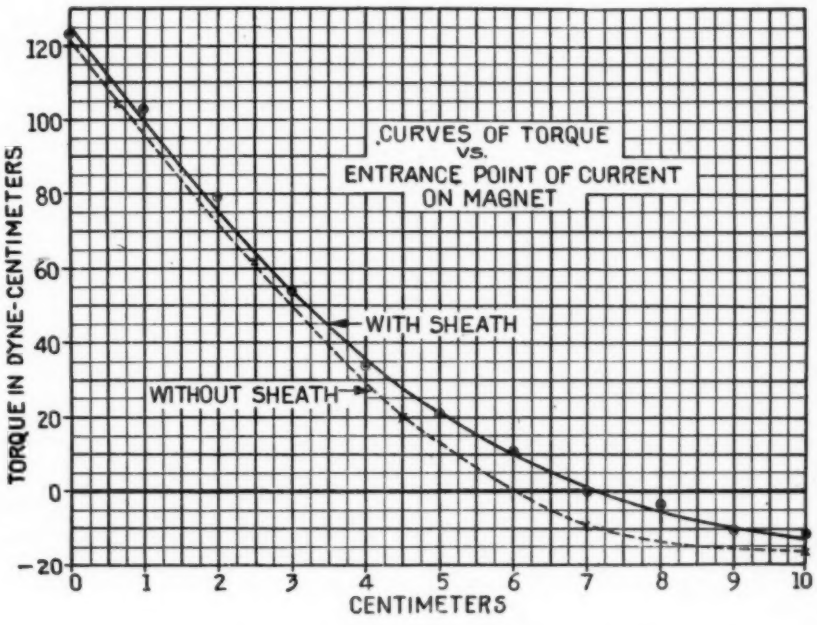


Fig. 2. Curves of torque with and without the sheath produced by varying the position of *B* of Fig. 1 from the tip of the magnet *D* to the middle point opposite *A*.

in the torque on the magnet arose when the current flowed through an insulated conducting sheath instead of in the magnet itself as in the experiments of Zeleny and Page. A series of values of the torque were observed for the current entering at a series of points along the magnet sheath 1 cm apart, beginning at the lower tip. The current in every case flowed out from the end of the horizontal arm. The same series was repeated with the sheath removed as a comparison. Fig. 2 shows the two curves of torque plotted against distance from the lower tip of the magnets. The curves are substantially alike, as indeed would be expected from the theory of the experiment. In both cases, the torque is zero when the current enters and leaves the magnet on the same surface of symmetry which coincides with the magnetic lines. Under the condi-

tions of the experiment, the small difference between the curves can be explained by a slight dissymmetry of magnetization. The maximum possible torque which arises when surfaces A and B include the entire flux of the magnet is given by the sum of the maximum positive and negative ordinates of the curves which is the same for the two cases. Incidentally using this torque and the corresponding current, the total flux from this magnet is found from Eq. (13) to be 29600 maxwells, giving a strength of pole of 2360 c.g.s. units.

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July 2, 1926.

ON THE CONFIGURATION OF A LORENTZ ELECTRON MOVING ARBITRARILY ALONG A STRAIGHT LINE

By S. C. Wang

Abstract

In the first part of the paper, by a natural extension of the contraction hypothesis of a Lorentz electron in uniform motion to the case of arbitrary linear motion, a differential equation is obtained of the form $(\partial x/\partial \alpha)^2+(\partial x/\partial u)^2=1$, (where $u=ct$, α and x are the distances of a point of the electron from its center when it is at rest and when in motion respectively). It is then shown that this differential equation is invariant under a Lorentz transformation. In the second part the exact solution of this equation is obtained, satisfying also the condition that the motion of the center of the electron shall be $x=$any given function of u.

WHEN a Lorentz electron is moving with a constant velocity βc, it is supposed to shrink to an oblate spheroid so that the dimension of the electron along the direction of motion is in the ratio $(1-\beta^2)^{\frac{1}{2}}:1$ to the original, while the dimensions perpendicular to the motion remain unchanged. Little has been discussed, however, regarding the shape of the electron in other kinds of motion. It is the object of this paper to make the most natural extension of our supposition to the case of linear motion with the distance as an arbitrary function of time and to obtain an exact solution of the problem so formed.

Part A

In the case of linear motion since there is an axial symmetry about the line of motion, it seems very plausible to assume that the dimensions perpendicular to the motion remain constant; the problem is therefore one-dimensional. We will use x as the coordinate along the direction of motion and referred to a fixed origin. Next we will assign a parameter α to the planes imbedded in the electron and parallel to the y-z plane; it is to be measured by the distance from the plane to the center of the electron at rest. For the time coordinate we will use u $(=ct)$.

Then for any point of the electron in a certain α-plane, the x coordinate at a time u will be a certain function of α and u; thus $x=x(\alpha, u)$. The velocity of the point α, divided by c, is

$$v/c=\partial x(\alpha,u)/\partial u$$

In the case of an electron moving with a uniform velocity βc, the x coordinates of any two points α_1 and α_2 are related thus:

$$x_1-x_2=(\alpha_1-\alpha_2)(1-\beta_2)^{\frac{1}{2}} \text{ or } \left(\frac{x_1-x_2}{\alpha_1-\alpha_2}\right)^2+\beta^2=1$$

The immediate extension of the above statement to the more general case of linear motion is to apply the formula to an element $d\alpha$, whereupon it becomes[1]

$$(\partial x/\partial\alpha)^2+(\partial x/\partial u)^2=1 \tag{1}$$

which is the differential equation we propose for the electron in linear motion.

As a law of the property of the electron in motion and hence a law of electrodynamics, it is important to know whether it is invariant under a Lorentz transformation, as electrodynamical equations generally are. Let the Lorentz transformation be defined by

$$x=\frac{x'+\beta u'}{(1-\beta^2)^{\frac{1}{2}}},\ y=y',\ z=z',\ u=\frac{u'+\beta x'}{(1-\beta^2)^{\frac{1}{2}}}$$

The first question to ask is, naturally: How does α transform? We defined α as the distance from a plane, perpendicular to the direction of motion and imbedded in the electron, to the center of the electron when it is at rest. Hence the α' of that plane is its distance, measured on the moving system, from the middle of the electron when the latter appears at rest to the moving system. This distance, as measured on the fixed system, is equal to $\alpha(1-\beta^2)^{\frac{1}{2}}$, from the simple form of the contraction hypothesis. Measured on the moving system, it is $\alpha'=\alpha(1-\beta^2)^{\frac{1}{2}}/(1-\beta^2)^{\frac{1}{2}}=\alpha$.

The equation of motion of a point α in the fixed system is $x=x(\alpha, u)$. When expressed in terms of quantities in the moving system, it becomes

$$\frac{x'+\beta u'}{(1-\beta^2)^{\frac{1}{2}}}=x\left(\alpha', \frac{u'+\beta x'}{(1-\beta^2)^{\frac{1}{2}}}\right) \tag{3}$$

If this equation is solved for x', we would get

$$x'=x'(\alpha', u') \tag{4}$$

which is the equation of motion in the moving system.

We will now compute the value of $(\partial x'/\partial\alpha')^2+(\partial x'/\partial u')^2$. Differentiating Eq. (3), we have

$$\frac{dx'+\beta du'}{(1-\beta^2)^{\frac{1}{2}}}=\frac{\partial x}{\partial\alpha}d\alpha'+\frac{\partial x}{\partial u}\left(\frac{du'+\beta dx'}{(1-\beta^2)^{\frac{1}{2}}}\right)$$

[1]Although the writer is not aware of the law explicitly stated in this form in the literature, the idea of extending the simple hypothesis by applying to the linear element is by no means new. See, for instance, Page, Phys. Rev. 11, 392 (1918).

$$dx'=\frac{(1-\beta^2)^{\frac{1}{2}}\partial x/\partial\alpha}{1-\beta\partial x/\partial u}d\alpha'+\frac{\partial x/\partial u-\beta}{1-\beta\partial x/\partial u}du'$$

Hence

$$(\partial x'/\partial\alpha')^2+(\partial x'/\partial u')^2=\frac{(\partial x/\partial\alpha)^2+\beta^2[1-(\partial x/\partial\alpha)^2]+(\partial x/\partial u)^2-2\beta\partial x/\partial u}{(1-\beta\partial x/\partial u)^2}$$

By the relation $(\partial x/\partial\alpha)^2+(\partial x/\partial u)^2=1$, the above reduces at once to

$$(\partial x'/\partial\alpha')^2+(\partial x'/\partial u')^2=1$$

We therefore see that this equation is invariant under a Lorentz transformation.

PART B

We will now proceed to solve this partial differential equation with proper initial conditions. The most useful form of the initial condition is probably that the coordinate of one point (say the mid-point) of the electron shall be a given function of time. Our problem is then to find a solution $x(\alpha, u)$ for the time interval u_1 to u_2, satisfying the partial differential equation and also the identity

$$x(0,u)\equiv f(u),$$

where $f(u)$ is a given function of u for the time interval considered.

The given differential equation can be solved for $\partial x/\partial\alpha$, giving

$$\partial x/\partial\alpha=(1-(\partial x/\partial u)^2)^{\frac{1}{2}} \tag{5}$$

(the case with the negative sign before the radical could not arise without passing through the transitional stage with a velocity equal to that of light).[2] For all physically permissible values of $\partial x/\partial u$ ($|\partial x/\partial u|<1$), our problem, with the initial condition as stated, constitutes what is known as a Cauchy problem,[3] and we know there is a unique solution.

It happens that this particular problem can be readily solved by the well known method of Lagrange.[3]

By mere inspection it is easy to see that the following is an integral

$$x=au+\alpha(1-a^2)^{\frac{1}{2}}+b$$

which contains two independent arbitrary constants a and b. It, therefore, affords all that is needed to obtain the most general solution. Proceeding in the usual way in solving a problem by the Lagrange's

[2] It might perhaps be less ambiguous to use Eq. (5), instead of Eq. (1), as the basic differential equation.

[3] Goursat-Hedrick, Mathematical Analysis, Vol. 2, 53 and 246, also 236.

method, we first put $b=\phi(a)$, where ϕ is an unknown function to be determined later, and get

$$au+\alpha(1-a^2)^{\frac{1}{2}}+\phi(a)-x=0 \tag{6}$$

Differentiating Eq. (6) with respect to a, we have

$$u-a\alpha/(1-a^2)^{\frac{1}{2}}+\phi(a)=0 \tag{7}$$

If the form of function ϕ is known, Eqs. (6) and (7) form a simultaneous system from which we can eliminate a and obtain x as a function of α and u; it is important to realize that in this system a is to be regarded as a function of α and u.

To determine the form of ϕ, we use the given initial condition

$$x(0,u)\equiv f(u) \tag{8}$$

Putting $\alpha=0$ in Eq. (6) and substituting into it the above value of $x(0, u)$, we get

$$ua(0,u)+\phi[a(0,u)]-f(u)\equiv 0 \tag{9}$$

Putting $\alpha=0$ in Eq. (7), we have

$$u+\phi'[a(0,u)]\equiv 0 \tag{10}$$

Differentiating Eq. (9) with respect to u, we have

$$a(0,u)+u\cdot\partial a(0,u)/\partial u+\phi'[a(0,u)]\cdot\partial a(0,u)/\partial u-f'(u)\equiv 0 \tag{11}$$

From Eq. (10) and Eq. (11), we obtain at once

$$a(0,u)\equiv f'(u) \tag{12}$$

Substituting this value of $a(0, u)$ into Eq. (9) and transposing,

$$\phi[a(0,u)]\equiv f(u)-uf'(u) \tag{13}$$

At this point we have to go a little into the detail of the nature of the function $f(u)$. We shall suppose that $f(u)$ possesses all the continuity and differentiability properties as far as we need them and, furthermore, that the time interval u_1 to u_2 under consideration can be divided into a finite number of subintervals each of which belongs to one of the following two classes:

(1) on the subinterval $f''(u)$ never vanishes, with the possible exception of the end points,

(2) on the subinterval $f''(u)$ vanishes identically.

Accordingly we divide the given interval of our problem into such subintervals and proceed to consider the solutions of the differential equation on them separately.

On subintervals of class (1) it is easily seen that the required solution is

$$x=\beta u+\alpha(1-\beta^2)^{\frac{1}{2}} \tag{14}$$

Since $f''(u)\equiv 0$, it means $f'(u)=\beta=$ a constant; it is then obvious that the differential equation as well as the initial condition is satisfied by the above solution.

On subintervals of the class (2), since $f''(u)\neq 0$ in the interior of the interval, $f'(u)$ is a monotonically increasing or decreasing function of u; the equation $a(0,\ u)=f'(u)$ (Eq. 12) can therefore be solved for its inverse

$$u=\psi[a(0,u)], \quad \text{so that } f'[\psi(a)]\equiv a \tag{15}$$

where ψ is a single-valued, continuous and monotonically increasing or decreasing function of its argument $a(0,\ u)$ in the subinterval.

The relation between u and $a(0,\ u)$ is therefore such that we can make a legitimate change of variable from u to $a(0,\ u)$. In terms of the new variable $a(0,\ u)$, Eq. (12) becomes

$$\phi[a(0,u)]\equiv f\{\psi[a(0,u)]\}-\psi[a(0,u)]\cdot f'\{\psi[a(0,u)]\}$$

Or, briefly,

$$\begin{aligned}\phi(a)&=f\{\psi(a)\}-\psi(a)\cdot f'\{\psi(a)\}\\&=f\{\psi(a)\}-a\psi(a)\end{aligned} \tag{16}$$

Similarly Eq. (10) becomes

$$\phi'(a)=-\psi(a) \tag{17}$$

Substituting the value of $\phi(a)$ and $\phi'(a)$ given by the above two equations into Eqs. (6) and (7), we get

$$x=au+\alpha(1-a^2)^{\frac{1}{2}}+f\{\psi(a)\}-a\psi(a) \tag{18}$$

$$u=\frac{a\alpha}{(1-a^2)^{\frac{1}{2}}}+\psi(a) \tag{19}$$

Eliminating the u in (18) by means of (19), we have

$$x=\frac{\alpha}{(1-a^2)^{\frac{1}{2}}}+f[\psi(a)] \tag{20}$$

Here, by eliminating a between Eqs. (19) and (20), we could obtain x as a function of α and u explicitly. Since, however, such an elimination is rarely practicable, we shall regard (19) and (20), which make use of the additional parameter a, as the final form of the solution on subintervals of class 2. In these equations $f(u)$ is the coordinate of the

center of the electron as a given function of time, and ψ is derived from f by the identity (15).

The complete solution of the problem for the whole time interval is the assemblage of solutions on the subintervals of the form given by Eq. (14) or by Eqs. (19) and (20), according to the class to which the subinterval in question belongs.

Professor Page has kindly informed me of the following criterion sometimes used to define the shape of the electron in motion: At any instant the electron shall appear to be spherical when measured (both regarding distance as well as time) on the system moving with the velocity which the center of the electron possesses at that instant. By a somewhat lengthy calculation it was found that the solution obtained above satisfies this criterion. It therefore follows that this criterion and the differential equation proposed above are equivalent.

I desire to take this opportunity to thank Professor L. Page for taking the pains to read over the manuscript and for offering valuable suggestions. I also want to express my gratitude to Dr. J. C. Slater. It was in his course on relativity that this problem was first suggested to me and the original of this paper was submitted as a term paper in that course.

HARVARD UNIVERSITY,
CAMBRIDGE, MASS.,
June 26, 1926.

ACOUSTICS OF THE PIANOFORTE

By R. N. Ghosh

Abstract

The amplitudes of fundamental and overtones of a steel string struck by a hammer as a function of time of contact. Vibration curves of a steel string struck by a tape-check system hammer taken from a piano were photographed and analyzed. The duration of contact between hammer and string was also measured photographically. The time of contact was varied by varying the striking position on the string and by varying the mass of the hammer. It was found that the amplitudes of the fundamental, the octave and the third harmonic were greatest when the time of contact was half the free period of vibration of the string.

The factors which determine the *choice of striking point* are discussed.

THE author has shown in a series of papers[1] that the duration of contact of the hammer with the string during impact depends upon the elasticity of the hammer, its mass and the striking distance. In this paper a short account is given of the experimental work on the amplitudes of partials for (1) the same hammer at different striking distances, and (2) for the same point by different hammers. The results show that the amplitude of the fundamental is a maximum when $T/\phi = 2$ or 1, where T is the free period of vibration of the string and ϕ is the duration of contact.

Experimental Methods

A steel string was fixed over two bridges in a sonometer kept vertical by suitable supports and the string was struck by a tape-check system hammer and key which were taken out of a piano for the purpose. The velocity of impact was kept constant by a mechanical device consisting of an eccentric wheel fixed just over the key. When the wheel was rotated it pressed the key once in a revolution. It was so arranged that a heavy load (1 kg) fell through a constant distance and gave only one revolution to the wheel. The point struck was photographed by a falling plate. To obtain the duration of contact in addition to the vibration curves the initial stages were simultaneously photographed with the trace of a vibrating tuning fork. In these experiments one precaution should be taken about the arrangement of the hammer system. The distance

[1] R. N. Ghosh, Phil. Mag. **47**, 1125 (1900); Proc. Ind. Assoc., Calcutta, **9**, III, 194 (1925). See also reference 3.

of the hammer from the string in the rest position should be such that when the former is slowly pressed it just comes near the string but does not press it. This is the arrangement in the piano.

The vibration curves were magnified fifty times and then a trace was taken. They were then analyzed by the schedule method given by

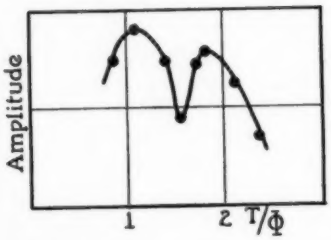

Fig. 1. Length of the string $l=100$ cm, freq. $=84$, $\rho=.096$ gr/cm, velocity of impact $=2\times10^4$ cm/sec.

Professor H. O. Taylor.[2] A large number of curves was obtained and analyzed. Below is given a graphical representation of a few typical sets, obtained with a single hammer. The time of contact (ϕ) was varied by varying the striking point.

George[3] has plotted the amplitude of the fundamental with respect to the striking distances α, but no definite results could be obtained.

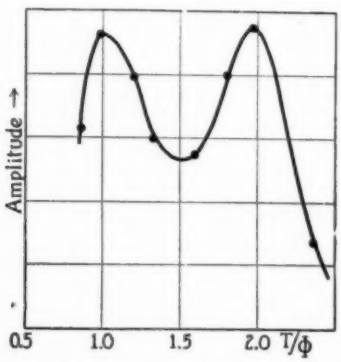

Fig. 2. $l=100$, freq. $=75$, $\rho=.0961$/cm, $\alpha=18$ cm, constant velocity $=2\times10^4$ cm/sec.

Curve (1) shows the relation between the amplitude of the fundamental and T/ϕ. In the figure the amplitude is shown qualitatively as a function of the striking distance. A large number of observations were made and graphs drawn, but in each case the curve as related to T/ϕ was the

[2] H. O. Taylor, Phys. Rev. **6**, 303 (1915).
[3] George, Phil. Mag. **50**, 491 (1925).

same. It will be observed that the amplitude reaches a maximum when $T/\phi=2$ or 1. It has been found that the amplitude of the octave and the third harmonic also follow the same rule. But the amplitudes of the octave and the third harmonic are greater at $T/\phi=2$ than for $T/\phi=1$.

If the amplitude is a function of the ratio T/ϕ, then it is to be expected that a variation of the ratio keeping the striking distance the same by using different hammers should show the same result as shown in curve (1).

Fig. 2 shows the relation between the amplitude of the fundamental (upper curve), and T/ϕ for a fixed striking distance. In all these cases T/ϕ was experimentally obtained. The second curve shows the same relation for the octave.

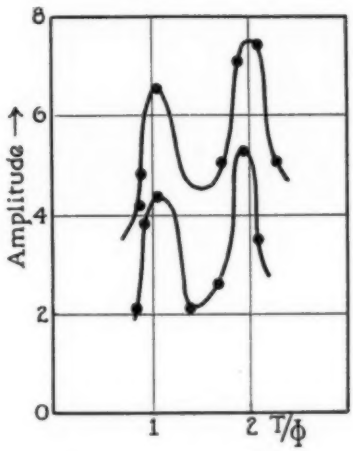

Fig. 3. $l=100$, $\rho=.0971$/cm, F = 88, $\alpha=20$ cm, constant velocity $=2\times10^4$ cm/sec.

Fig. 3 shows the same relations, with a striking distance of 20 cms. From these experiments we therefore conclude that the amplitudes of the fundamental, the octave and the third harmonic are at their maxima when $T/\phi=2$. They are large again at $T/\phi=1$.

Choice of the Striking Point

In general the striking point in the piano varies from $l/7$ to $l/9$ in the bass section, and $l/20$ in the treble section. The hammers also vary in mass in different octaves, they are lighter in the higher octaves. From a musical point of view the choice of the striking point should be such that the first few harmonics should be present in considerable force. We have seen the first three components have maximum amplitude

when $T/\phi=2$. Hence the choice of the hammer mass and the striking distance should be such as to insure this condition. Now

$$T/\phi=\frac{T}{\pi}\left(\frac{T}{M}\right)^{\frac{1}{2}}\left(\frac{1}{\alpha(1+T/\mu\alpha)}-\frac{\rho}{4M}\right)^{\frac{1}{2}} \qquad (1)^4$$

where T is the tension, M the mass of hammer, μ its elasticity. Now from Eq. (1) we see that T/ϕ mainly depends upon the product $M\alpha$ which is now fixed for the particular ratio, *viz.* $T/\phi=2$.

Now α should not be very small for then the resulting amplitude of vibration of the string will be small since it depends upon the factor $\sin(s\pi\alpha/l)$.[5] It cannot be very large for then the reflections from the farther end will produce double contact which is detrimental to the production of a good note. Hence α is fixed between two wide limits. But since the character of the musical note depends also upon the convergency of the component tones, α is fixed. The convergency factor or the music factor for $T/\phi=2$ is given below

$$F=\sin m,\ \frac{\sin 2m}{6},\ \frac{\sin 4m}{60},\ \frac{\sin 6m}{210}\cdots \qquad (2)^5$$

$$m=\pi\alpha/l.$$

Once the music factor is determined from the tone quality, α/l is fixed, and then M is calculated from Eq. (1). Thus we see that the choice of the striking point and the mass of the hammer must satisfy the following conditions

$$T/\phi=2,\quad M\alpha=\text{const},\quad F=\text{music factor} \qquad (3)$$

The striking point is usually closer to the fixed bridge. The reason for this is to minimize the free vibrations of the bridge and the board as far as possible, and to prevent the reflections from the bridge, and the slight variations[6] of pressure during contact, the effect of which is to render the tone unmusical.

The author has taken a large number of photographs of the vibration curves when the hammer, the striking point, and the velocity of impact were all kept constant, *but the nature of the impact was changed.* No change in the vibration was found. This is in accordance with the conclusions arrived at by Professor Miller that the tone quality cannot be changed by emotional touch of the key. As long as the position of the hammer is invariable, tone quality cannot be changed.

[4] R. N. Ghosh, Phys. Rev. **24**, 456 (1924).
[5] Rayleigh's Theory of Sound, Vol. 1, p. 190.

Double Contact

Fig. 4 shows that the hammer once left the string and again came in contact with it finally leaving it when the pressure became zero. When the distance of the striking point from the nearer end is small, the duration of contact is less than $T/2$, and the hammer remains in contact with the string throughout the time of contact. Under this condition the wave generated by impact does not reach the farther end before the impact is over. The reflections from the nearer end may lead to slight variations of pressure as mentioned before. It is easy to show[6] that the string attains a velocity greater than the hammer when reflection takes place from the farther end provided the duration of contact is so large.

Fig. 4.

Let us take a case when the total duration of contact is approximately the same as the free period of vibration of the string, so that the hammer remains in contact when the wave is reflected from the farther end. At the point of impact the displacement of the string is given by

$$y = Ae^{-Kt/2} \sin qt \quad \pi/q = T(\text{approx}) \tag{4}$$

The equation of the wave motion towards the longer side before reflection is

$$y = Ae^{-K(ct-x)/2c} \sin q(ct-x)/c \tag{5}$$

As long as the impact lasts the velocity of the hammer is given by

$$v_h = ARe^{-Kt/2} \cos(qt+\psi) \tag{6}$$

The equation to the reflected wave is given by

$$y_r = -Ae^{-K(ct+x-2l)/2c} \sin q(ct+x-2l)/c \tag{7}$$

[6] Curves by Professors Raman and Banerji, Proc. Roy. Soc. 97, 99 (1920).

The velocity of the hammer continues to be represented by (6), but after reflection the velocity of the string at the point of impact is $\dot{y}+\dot{y}_\gamma = v_s$ and

$$v_s = ARe^{-Kt/2}(2+KT/2)\cos qt \text{(neglecting } \psi) \tag{8}$$

From (6) and (8) we find that the velocity of the point on the string is greater than that of the hammer and therefore leaves it. When the point returns after approximately a time $T/2$ the velocity

$$v_s = -ARe^{-K(t_1+T/2)}(2+KT/2)\sin \pi t_1/T \tag{9}$$

$$t_1 = t - T/2$$

The velocity of the hammer at the same instant is

$$v_h = -ARe^{-K(t_1+T/2)}\sin \pi t_1/\mathrm{T} \tag{10}$$

Thus we see from (9) and (10) that the point moves faster than the hammer, and therefore overtakes it.

In a subsequent paper the author proposes to discuss the nature of vibration of the piano string, and the sound board as coupled together.

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ON THE LARGE MOTION OF THE NODES OF A STRING AND AN AIR COLUMN

By Satyendra Ray

Abstract

From the result that the velocity of a wave cannot be independent of the amplitude of vibration the large motion of nodes of strings discovered by Raman is explained as well as the drift motion of lycopodium dust in Kundt's tube experiment.

PROFESSOR C. V. RAMAN has recorded some very interesting observations on the small vibration of nodes.[1,2] The "small vibration" is small only in so far as the transverse part of the vibration is concerned, the longitudinal part, which also exists, being of very large amplitude, as Professor C. V. Raman himself points out. He says,—"On account, however, of the small transverse motion at the nodes, the points of intersection (of two opposite phases of the actual motion of the string) or 'fictitious nodes' are seen to execute a motion of large amplitude parallel to the string—the range of motion being equal to the whole length of a loop."

In Sec. II on the "small motion at the nodes of a vibrating string"[2] are given photographs of 13 stages of the motion of the string (each giving two opposite phases of the motion of the string, as in the photographs in the PHYSICAL REVIEW. These photographs are described in the following words: "It will be seen that the point of intersection or 'node' which is first in the center moves off to one side of the field, *first slowly and then more quickly*, till after the lapse of a time which can be seen to be exactly half the period of the cycle it has gone well off the plate and the two positions of the string seen in the photograph are sensibly parallel. Direct observation shows that the point has moved off to a distance equal to half the length of a segment. It simultaneously appears at an equal distance on the other side and moves in from that direction first quickly and then more slowly till it reaches the center again, and the cycle is complete."

The longitudinal motion of the node has therefore an amplitude equal to $\lambda/4$. This longitudinal motion is moreover not of the S.H.M. type. From what has been quoted, and more especially from the photograph, the equation for this longitudinal motion appears to be approximately of the form

[1] Raman, Phys. Rev. **32**, 309 (1911).
[2] Raman, Researches in Acoustics.

$$x = a\tan 2\pi t/\tau \tag{1}$$

instead of the usual form

$$y = b\cos 2\pi t/\tau \tag{2}$$

which is apparently still true for the transverse component. In the form of Eqs. (1) and (2) the phase relationship of the two motions indicated by the photographs has been taken into account. If $\sqrt{x}$ and $\sqrt{y}$ be plotted parallel to the axis of $x+y$, the locus of $\sqrt{x}$, $\sqrt{y}$ would describe a hyperbola $xy+ay-ab=0$ having its asymptotes parallel to the axes. The x-component is however hardly of the nature of a stationary vibration, the point flying off to infinity and then coming back to the center from infinite distance on the opposite side, the direction of the motion remaining always the same. Such a motion is certainly not amenable to Fourier's analysis.

Professor Raman gives a general explanation of the phenomenon discussing only the "small motion." He writes:—"The explanation of these phenomena is that the small motion at the node is not in the same phase as the large motion elsewhere. It is evident from the photograph that the small displacement at the node is a maximum when the large motion elsewhere is a minimum: in other words, that its phase differs by exactly a quarter of a period of the vibration from that of the general motion of the string. The sign of the phase of the small motion at any node may be found from the following rule, which is verified by observation. If the tuning fork which imposes the obligatory transverse motion is exactly at a node, it is opposite in phase to the small motion at the next node, and in the same phase as the motion at the node next after that, and so on." (Researches in Acoustics, Sec. II, p. 9.) An independent method of demonstrating that the small motion differs in phase by a quarter of a period is given in Sec. I of "Researches in Acoustics," as well as in the PHYSICAL REVIEW. The equation

$$y = \frac{V\sin\theta}{R^2}\left\{\sin\alpha x\cos pt + \frac{kx}{2\alpha}\cos\alpha x\sin pt\right\}$$

is given as "containing in a nut shell the complete theory of the transverse small motion." The theory of the longitudinal motion of the node has however not been investigated by Professor C. V. Raman though accurate observations and beautiful photographs illustrating the nature of the longitudinal motion have been recorded and published.

In the present paper the longitudinal motion of the node is investigated from a very simple but fundamental principle which has been shown by

the present author to be valid in the case of vibration of "ether" strings.[3] It has been shown that, for light of all wave-lengths to travel with the same velocity, α/λ must be a constant. The same relation can easily be proved for waves along a string. Now the stationary vibration of the string is regarded as the superposition of two waves traveling in opposite directions. In the ordinary case we assume

$$y = a\sin 2\pi(t/\tau - x/\lambda) + a\sin 2\pi(t/\tau + x/\lambda)$$
$$= [2a\cos 2\pi(x/\lambda)]\sin 2\pi(t/\tau)$$

to give the stationary vibration of a string.

Now let the tuning fork send a wave along the string from left to right, given by

$$y = a\sin 2\pi(t/\tau - x/\lambda)$$

The reflection will be a wave given by

$$y = a_1\sin 2\pi(t/\tau - x/\lambda_1)$$

where both a and λ are different from a_1 and λ_1 on account of absorption of energy at the reflecting wall on the right. As the "large motion" of the node of the string *is due to the phase difference resulting from the difference in the value of* λ, we can as a first approximation, neglect the small difference between a and a_1, and take into consideration the difference of λ only. We have then for the stationary vibration

$$y = a\sin 2\pi(t/\tau - x/\lambda) + a\sin 2\pi(t/\tau + x/\lambda_1)$$

which immediately gives the motion of the node parallel to the x-axis as a result of the variation of the velocity, and therefore of the wave-length, of the two interfering waves. This fact indeed is pointed out by Professor Raman himself though in slightly different language. He says that the result of his mode of attachment of string to fork prong is that the "frequencies of vibration in the two planes at right angles differ slightly and this has the desired effect of keeping the two component vibrations confined to their respective planes, if the tension of the string lies anywhere within a definite range." Obviously the apparent change in frequency, regarded necessary for the maintenance of the vibration, can be attributed to difference in velocity or wave-length if the frequency be taken constant.

This can be shown in another way. For the stationary vibration the transverse motion is given by Professor Raman in the form:

$$y = A\sin\alpha x\cos pT + B x\cos\alpha x\sin pT \qquad (3)$$

[3] Ray, Zeits. f. Physik **8**, 112 (1922).

This can be thrown into the form:

$$y=\tfrac{1}{2}A\sin(\alpha x+pT)+\tfrac{1}{2}A\sin(\alpha x-pT)$$
$$+\tfrac{1}{2}Bx\sin(\alpha x+pT)+\tfrac{1}{2}Bx\sin(pT-\alpha x) \qquad (4)$$

which means that on two "waves of constant type," travelling in opposite directions, two waves of variable amplitude moving in opposite direction are superposed. In the second case the amplitude is proportional to the distance from the fixed end for both the positive and negative waves. This becomes, indeed, obvious if we consider an extremely slow motion of the string to and fro with the prong, without considering the wave generated. The string would sweep through a small angle and each point would, on account of this "bodily motion" of the string, describe a periodic motion with an amplitude proportional to the distance from the fixed end. The wave is superposed on this motion.

To find the large vibration parallel to the string we put, for the stationary vibration:

$$y=a\sin 2\pi(t/\tau-x/\lambda)+a\sin 2\pi(t/\tau+x/\lambda_1)$$

where $\lambda_1<\lambda$. Hence,

$$y=a\sin 2\pi(nt-mx)+a\sin 2\pi(nt+m'x)$$

where $n=1/\tau$, $m=1/\lambda$, $m'=1/\lambda=m+dm$.
Hence, since dm is small we have approximately

$$y=[2a\cos 2\pi mx]\sin 2\pi nt+[2\pi axdm]\cos 2\pi(mx+nt)$$
$$=[2a\cos 2\pi mx]\sin 2\pi nt-[2\pi ax(d\lambda/\lambda^2)]\cos 2\pi(mx+nt) \qquad (5)$$

which gives the superposition of a progressive wave on a stationary vibration. For a node we have $y=0$. The nodes therefore satisfy the relation

$$\cos 2\pi mx\sin 2\pi nt=[\pi x(d\lambda/\lambda^2)]\cos 2\pi(mx+nt$$

and therefore

$$\sin 2\pi nt\{\cos 2\pi mx+\alpha\sin 2\pi mx\}=\alpha\cos 2\pi mx\cos 2\pi nt$$

where

$$\alpha=\left[\pi x\frac{d\lambda}{\lambda^2}\right] \text{ or}$$

$$\lambda^2/\lambda xd\pi+\tan 2\pi mx=\cot 2\pi nt$$

or putting $\lambda^2/\pi xd\lambda=N$ where N is a large number

$$N/\pi x\lambda+\tan 2\pi mx=\cot 2\pi nt$$

or

$$x=N\tan 2\pi nt+x\tan 2\pi mx\tan 2\pi nt. \qquad (6)$$

If we neglect the second term of the right hand expression it reduces to the form which the photographs in "Researches in Acoustics" suggests to the eye. It is a periodic motion only formally and not of the simple harmonic type. Over it is superposed another term which is, formally, similar to the stationary vibration formula for transverse motion, but is of the same open type as the last one.

To find the amplitude of the vibration we can throw it into the form

$$\tan 2\pi nt = (N/x + \tan 2\pi mx)^{-1} \tag{7}$$

When $t=0$, $x=0$ satisfies the equation. After a quarter period the position of the node is given by $N/x = -\tan 2\pi mx$ or

$$N = -x\tan 2\pi mx \tag{8}$$

If x is positive $\tan 2\pi mx$ must be negative, and for a value a little over $\frac{1}{4}\lambda$ the relationship will still be satisfied. The maximum excursion on the negative side will be a little under $\frac{1}{4}\lambda$. The motion is therefore not perfectly symmetrical, as Eq. (1) at first sight seems to be. The actual equation has, however, the advantage of making the amplitude of the large vibration "finite" and equal to the quantity $\frac{1}{4}\lambda$ found experimentally by Professor Raman. Also there is experimental evidence of the slight asymmetry of the motion in the stroboscopic photographs in the "Researches in Acoustics."

The velocity of the node parallel to the string is easily found from Eq. (7). We have

$$-N dx/x^2 + 2\pi m \sec^2 2\pi mx dx = -2\pi n \operatorname{cosec}^2 2\pi nt dt$$

Therefore

$$\frac{dx}{dt} = \frac{2\pi n \operatorname{cosec}^2 2\pi nt}{N/x^2 - 2\pi m \sec^2 2\pi mx} \tag{9}$$

$$= \frac{x^2}{N - x^2 2\pi m \sec^2 2\pi mx} + \frac{2\pi}{(N/mx^2 + 2\pi)\tan^2 2\pi nt - 2\pi \tan^2 2\pi mx \tan^2 2\pi nt}.$$

This makes the velocity zero at $x=0$, but enormously large for positive and negative values of displacement from this position. This explains by the persistence of vision the appearance of the node at the points where it is expected from the elementary consideration, when in reality it is describing (formally) about this position, a vibration of amplitude of $\frac{1}{4}\lambda$ parallel to the length of this string. Of course, it is a question if it is

permissible to call it a vibration when the direction of the motion is always the same and is never anywhere reversed during the period of vibration.

The node really possesses a progressive motion away from the source of energy, the velocity of the motion being periodically zero and very large depending upon the distance from the source of energy, the average velocity of the node being equal to the velocity of the wave along the string. (Cf. quotation from "Researches in Acoustics," Sec. II, p. 9 given earlier.)

The results of the above investigation hold also for stationary vibrations in air columns. The "large motion" of the node is met with experimentally in Kundt's tube experiment. A drift of lycopodium dust is found to take place from the source of energy to the fixed wall opposite. For example Barton observes "By a continued sounding of the rod's note, by stroking it, the dust figures should then *change slowly by a motion* in the ventral segments, *from the disk towards the stopped end of the tube*, until the dust is in little heaps at the nodes. This state, which is somewhat difficult to obtain, is shown in Fig. 83 of Barton's textbook on Sound, p. 369. This drift, indeed, is a well known fact, but one for which no explanation is given. The phenomenon is due to the motion of the node in an air column being a complete analogue of the large motion of the node in strings described by Professor C. V. Raman. The author is glad to place on record that Professor Raman has accepted the explanation given here of his experiment.

LUCKNOW UNIVERSITY,
February 6, 1926.

BOOK REVIEWS

General Physics for the Laboratory. L. W. TAYLOR, W. W. WATSON, and CARL E. HOWE.—"Three policies have predominated in the development of this book: the presentation of a fairly complete outline of the theory of each experiment; the inclusion only of experiments for which standard apparatus is procurable; the formulation of the laboratory instructions in a rather unusually specific and detailed way." In pursuance of these policies, the authors have presented the theory of each of the 49 experiments in such form that it may be assigned for study and for classroom discussion. This has necessitated the omission of a number of familiar experiments that one rather expects to find, at any rate if the manual is to be used for first-year students. Among such experiments are those on the compound pendulum, friction, melting points and heat of fusion, resistance measurement by other means than the Wheatstone bridge, the simple lens, mirrors, and thermoelectricity. On the other hand a summary of alternating-current theory is given in connection with the measurement of self-inductance, and there is an excellent experiment on the characteristics of thermionic vacuum tubes; no mention is made, however, of oxide-coated or thoriated filaments. The experiments on optics are particularly good. There are a few instances in which the text might be improved by the addition of a little more detail. Thus in the experiment on the Wheatstone bridge, no reason is given for closing the battery key first, nor for interchanging the positions of the unknown and known resistances; units are not always clearly specified; under "Measurement of Capacitance" we read "experience shows that for most galvanometers the ratio ρ of successive damped swings is almost a constant": in view of the importance of the decrement of oscillating systems reference should also be made to the simple theory, according to which this quantity *is* constant. In this same experiment it is tacitly assumed that the galvanometer scale is circular, and that the deflection is proportional to Q. With reference to the decrement, it is only from the context that one knows whether the "successive swings" are in the same direction or not. Such minor defects as these do not detract seriously from the value of the book, which deserves high praise. The reviewer heartily approves of the policy of giving rather full directions for manipulation. The excellent photographs of apparatus should prove of great aid to the student. The book concludes with an appendix on trigonometry and on descriptions of various instruments. The customary tables are provided.—Pp. vi+247, 145 figs. Ginn and Co., 1926. Price $2.40.

W. G. CADY

A Handbook of Physics Measurements. (Second ed., revised). Vol. I, Fundamental Measurements, Properties of Matter and Optics. E. S. FERRY, in collaboration with O. W. Silvey, G. W. Sherman, Jr., and D. C. Duncan.—The new edition* of this excellent laboratory manual differs from the former one chiefly in the inclusion of a 17-page chapter on Color Analysis, with accompanying chart and tables. This chapter treats briefly, but very clearly, of such topics as the specifications of a color, fundamental color, excitations, and the color mixture triangle, and contains detailed instructions for the use of the Keuffel and Esser color analyzer. The only other new feature in this edition of the first volume is an appendix containing twenty-six interesting and suggestive "laboratory problems and projects". Otherwise the book is printed from the old plates, with the exception of the revision of a few numerical data in the tables. In common with most other laboratory manuals, this book gives no references to the sources from which

* For review of the first edition see Phys. Rev., **14**, 457 (1919).

the table of "constants" are derived. It seems to the reviewer desirable that such references should be given at least in cases when there is lack of agreement between different authorities. Attention may be called to two slight errors: the dealer in scientific apparatus named on page 189 has gone out of business since the appearance of the first edition; and near the foot of page 192 "Exp. 30" should read "Exp. 31."—Pp. xii+288, 162 figs., 18 tables. John Wiley & Sons, New York, 1926. Price $2.50.

W. G. CADY

Elements d'Astrophysique. ALBERT NODON.—This attractively prepared book, by the President of the Astronomical Society of Bordeaux, contains, in a small compass, a great deal of information about modern atomic and astrophysical theories, and a series of illustrations—many of them excellent—derived mainly from French sources. It has evidently been written by an enthusiastic lover of the subject, in the hope that others may be led to share his interest. Most regrettably, the presentation of current facts and theories is marred by many errors—some of which, but by no means all, can be attributed to the printer. Many of the illustrations are admirable in themselves; but there is often nothing in the text to explain them intelligibly to the ordinary reader. Considerable space is devoted to the presentation of certain conclusions of the author's regarding the ultimate nature of the ether, the origin of gravitation, and the like. These views are frankly presented as speculative, so that no criticism is in order, except to note that the hypothetical data—such for example as the number of ultimate particles in a cubic millimeter of ether, are given to four significant figures. Pp. viii+244, 42 figs., Librairie Scientifique Albert Blanchard, Paris, 1926. Price 20 frs.

HENRY NORRIS RUSSEL

The Elements of Internal-Combustion Engineering. TELFORD PETRIE.—The ever-growing importance of the gas engine in modern life makes it a subject with which the physicist needs at least a general familiarity. While this small volume is intended as a class room textbook, it will be found very readable and interesting in the descriptive parts, as well as simple and direct in the analytical part. The first three chapters are concerned with a description of the various types and their historical development. The diagrams used are somewhat unique in that they are very frankly not simplified constructional drawings but are very successful attempts to show only the necessary parts and mode of operation, so that the general situation may be quickly and vividly understood. The next two chapters develop the thermodynamic relations of the ideal gas and ideal cycles. These relations are applied in the following two chapters to the cases of constant and of variable specific heats. This leads up to the use of entropy, of entropy charts, and of the charts involving the other variables, which are such effective aids in the solution of these problems in terms of the complex properties of the working materials. The following three chapters are devoted to the problems of the formation of the explosive mixture, that is, carburetor and injector problems. The book closes with a short stimulating account of the probable future developments, among which the author expects the gas turbine to occupy a prominent place. The book is perhaps exceptional in its persistent reduction to arithmetical terms of each and every algebraic result. As a consequence, approximate solutions are continually discussed with their required or available accuracy. A large group of such arithmetic problems is given at the end of the book. xi+236 pp., 62 diagrams, Longmans, Green and Co., New York City, 1925. Price $3.75.

J. R. ROEBUCK

Principles of Physics. CHARLES C. BIDWELL.—"This text is a development from notes used for several years in mimeograph form by students of engineering and chemistry at Cornell University as a basis of a second course in physics. It is designed for those students who have completed an introductory course in college physics, and have had a first course in differential and integral calculus . . . . . The present volume is a

revision of the material previously published (1922) under the title *Outlines of Physics*. Numerous corrections and changes have been made and a considerable amount of new material added." This little book is chiefly a formulation and brief discussion of the chief laws of mathematical physics. Statics and the mechanics of liquids are omitted on the one hand, while on the other hand there is almost nothing on modern electron and atomic theory. For example, under magnetic induction, the author goes no further than to mention "magnetized molecules." There is less on some topics than in many first-year textbooks, as for example interference and diffraction. In the field covered, however, the book offers a well-written basis for more extended lectures to second-year students. The law of electromagnetic induction, p. 131, is commonly known as Neumann's Law, and not as Lenz's Law.—Pp. 230+ix, 182 figs. Comstock Publishing Co., Ithaca.

W. G. CADY

Numerical Drill Book on Physics. LLOYD WILLIAM TAYLOR.—The outstanding features of this excellent little book of problems are these: nearly every example is stated in algebraic terms, demanding an algebraic solution before numerical values are substituted; and four independent sets of numerical data are provided for each example, in a compact table which also contains the answers. The various numerical values are cleverly chosen so as to illustrate the course of phenomena under varying conditions, and can in many cases be used for the study of maximum or minimum effects. While the advantages of this plan are obvious, it invites the criticism that many of the problems tend somewhat to conform to one general type, requiring less reasoning ability than facility in selecting the right formula. Nevertheless, the problems are so well chosen, and illustrate the operation of important physical laws so convincingly, that the book should find a warm welcome among physics teachers. The more advanced problems demand very careful thought, and indeed some of them seem rather beyond the range of the average first-year student of college physics. On pp. 21 and 25 we note a conflict in statements concerning the numbering of problems using the English units and the metric units respectively. At the end of the book are a few mathematical and physical tables.—pp. viii+95, Ginn & Co., 1926. Price $1.00. W. G. CADY

Probleme der Atomdynamik. MAX BORN. (German edition of Professor Born's Massachusetts Institute of Technology Lectures).—The German edition of these lectures differs from the English primarily through the insertion of a brief sketch of recent solution of the problems of the complex structure of spectrum lines and of the complex Zeeman effect by Pauli and by Heisenberg and Jordan in terms of the new quantum mechanics and the Uhlenbeck-Goudsmit spinning electron hypothesis. The added material occupies only eight pages, but it represents a major victory for theoretical physics. The record of achievement to the credit of the new theory in the few short months since its conception is, indeed, nothing short of astounding.

The use of bold face type for matrix quantities in the German edition of these lectures adds not a little to the clarity and attractiveness of the text. An index has also been appended. Pp. VIII+183, 42 figures. Julius Springer, Berlin, 1926. Price 10.50 RM, 12.00 RM bound.

E. C. KEMBLE

Structure et Activitê Chimique. In April of last year, there was held the second called meeting of the Conseil de Chimie of that unique organization, the Institut International de Chimie Solvay. The topic set for discussion by the committee is indicated by the title of the present volume, which publishes the results of the council's work. It is set forth under the following sub-headings:—The Spreading of Liquids on Water and on Solids; Crystal Structure and X-Rays; Chemical Activity; Reactivity of Molecules.

Each topic is handled by individual reports and discussions, partly from the floor, and in some cases communicated, in the style familiar in the symposia of the Faraday Society. The discussions are full, and set forth without fear or favor.

The book is a mine of information and opinion for physicist as well as chemist, covering as it does that field between the atom and chemical reaction, which is of interest to both sciences. In order to make it clear that the reports are of importance, and that the discussion of the reports is worth reading, it is only necessary to point out that they represent the work, ideas, and opinions of men such as the following: Sir W. B. Hardy; the Braggs; M. J. Duclaux; T. M. Lowry; M. Tiffeneau; J. Perrin; E. K. Rideal; Euler, and others. In closing, it may be said that probably the most interesting report is Perrin's attempt at correlation of the mass law with a new statement of the radiation hypothesis, which called forth some sixteen pages of discussion, pro and con. The reviewer regrets that the absence of Tiffeneau prevented a discussion of his fine report on the influence of groups on reactivity, and on the inter-atomic ties in molecues.

Taken as a whole, there is no other single place known to the reviewer, in which there can be found the views of so many European scientists on these topics. It is to be hoped that when the committee calls another council the international aspect may be still further stressed by the inclusion of some Central European and North American scientists. Pp. XIV+672. Gauthier-Villars and Cie, Paris, 1926. Price 80 fr.

W. H. HUNTER

ERRATA

SMALL-SHOT EFFECT AND FLICKER EFFECT. Walter Schottky. Vol. 28, pp. 74–104. July, 1926.—

Pages 79–80, Figs.: The abscissas of Figs. 3 and 4 should be labelled "v" instead of "f."

Page 80, Fig. 4: An arrow 5 mm to the right of letter D is omitted.

Page 81, line 1 of footnote 8: should read "The cooling effect" instead of "This."

Page 88, line 10: should read t_1 instead of t^2.

Page 88, line 12: The expression on line 12 should be numbered (8).

Page 89, line 1: should read Eq. (9) instead of Eq. (7).

Page 89, Eq. (11): should read N_0 instead of N_1.

Page 90, line 3: should read t_1 instead of t_2.

Page 90, last paragraph: Omit "Since" and put "for" instead of "it follows, that."

Page 93, Figs. 6a and 6b: The figure labelled 6a should be 6b and vice versa.

Page 100, two lines before Eq. (29): should read θ_1 instead of θ.

Page 102, one line before Eq. (32′): should read Q_{00} instead of q_0.

Page 102, Eq. (33): should read M instead of 14.

PHYSICAL PROPERTIES OF WELL SEASONED MO AND TA AS A FUNCTION OF TEMPERATURE. A. G. Worthing. Vol. 28, pp. 190–202. July, 1926.—The radiation intensities for tantalum as given in Table IV, page 200, should be corrected to read as follows:

Temperature in degrees K	Radiation intensity η in watts/cm²
1600	7.3
1800	12.8
2000	21.2
2200	33.4
2400	50.7
2600	75.
2800	106.

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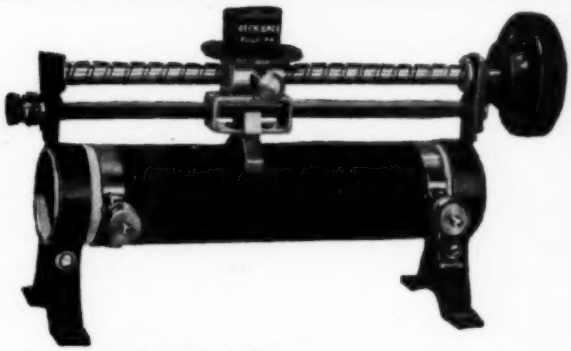

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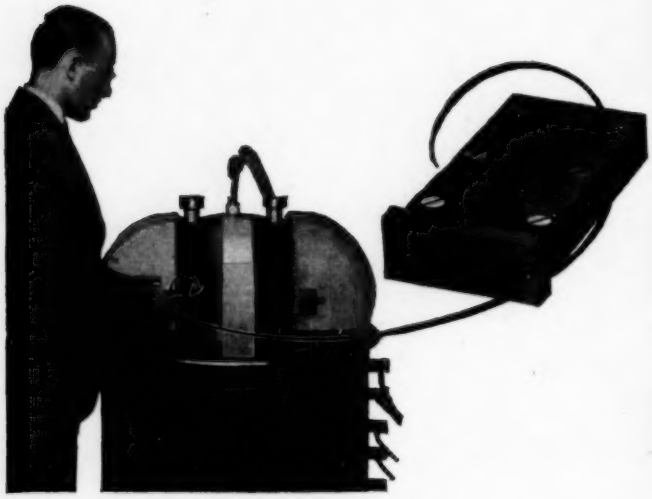

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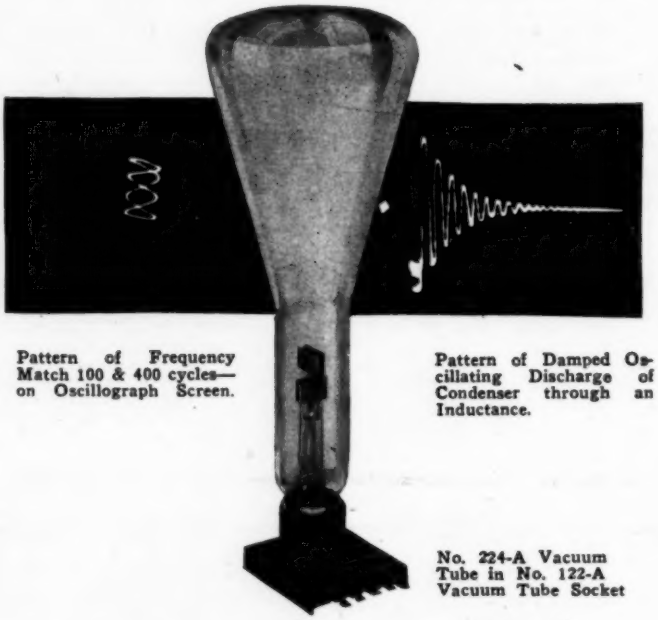

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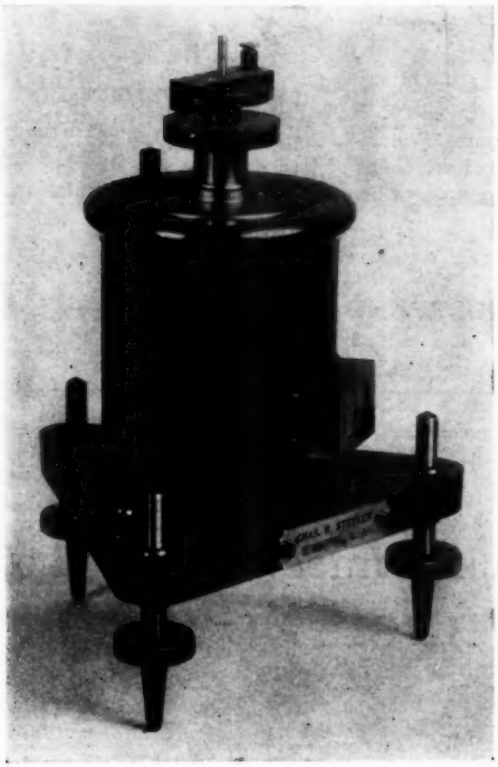

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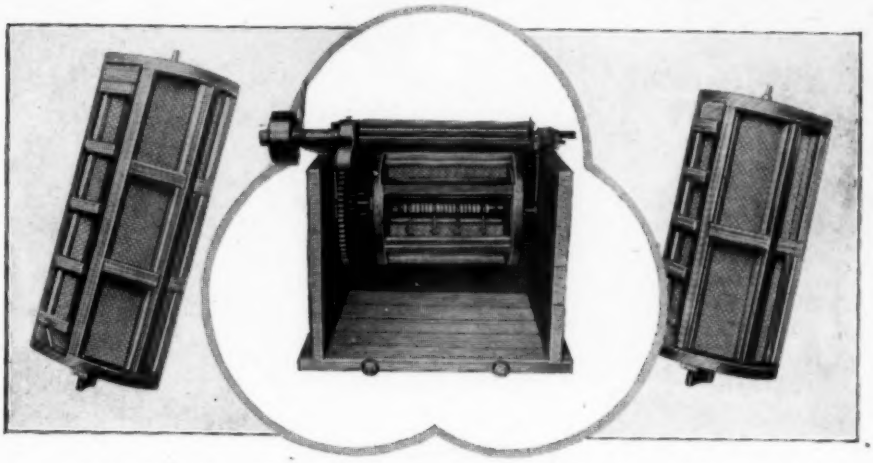

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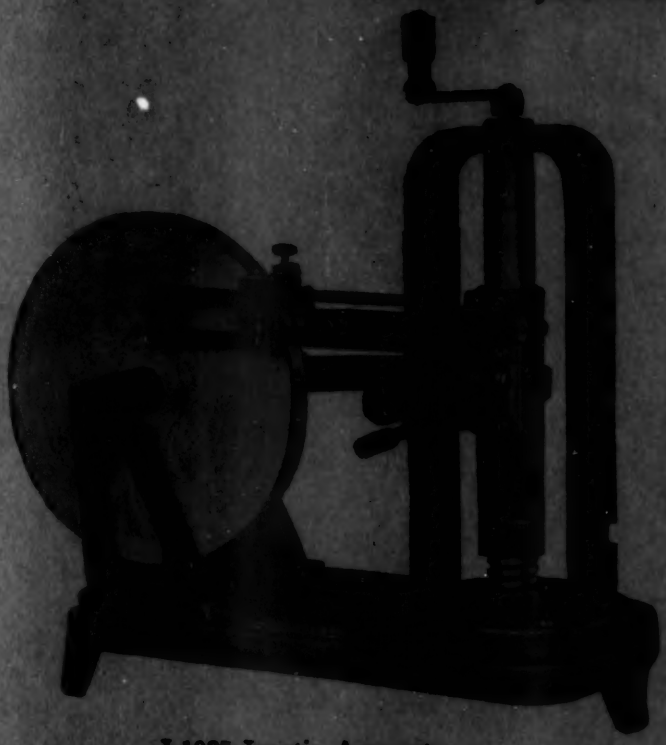

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